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A peroxynitrite complex of copper: formation from a copper–nitrosyl complex, transformation to nitrite and exogenous phenol oxidative coupling or nitration

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Abstract

Reaction of nitrogen monoxide with a copper(I) complex possessing a tridentate alkylamine ligand gives a Cu(I)–($\cdot$ NO) adduct, which when exposed to dioxygen generates a peroxynitrite ($\text{O}=\text{NOO}^-$)–Cu(II) species. This undergoes thermal transformation to produce a copper(II) nitrito (NO_2^-) complex and 0.5 mol equiv O_2 . In the presence of a substituted phenol, the peroxynitrite complex effects oxidative coupling, whereas addition of chloride ion to dissociate the peroxynitrite moiety instead leads to phenol *ortho* nitration. Discussions include the structures (including electronic description) of the copper–nitrosyl and copper–peroxynitrite complexes and the formation of the latter, based on density functional theory calculations and accompanying spectroscopic data.

Keywords

Copper-nitrosyl complex; Copper peroxynitrite; Biological copper; Density functional theory calculations; Phenol oxidation or nitration

Introduction

The interactions of nitrogen oxides (NO_x) with copper ion species are a subject matter of continuing research activity because of their fundamental relationship to biological and environmental processes [1–3]. For example, in bacterial denitrification, copper enzyme active sites effect nitrite (NO_2^-) reduction to nitrogen monoxide ($\cdot$ NO; nitric oxide) in nitrite

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reductase [1,4–6] and the transformation of N_2O to N_2 in nitrous oxide reductase [7,8]. Another important NO_x compound is peroxyxynitrite [oxoperoxonitrate (1-), $\text{O}=\text{NOO}^-$] [9–17], a powerful oxidant and nitrating agent involved in nitric oxide biochemistry and nitrosative/nitrative stress injury. It is most often discussed in terms of its formation by the near-diffusion-controlled direct reaction of $\cdot\text{NO}$ with superoxide anion ($\text{O}_2^{\cdot-}$), $k = 1.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ [12,13,18]. However, metal ions in biological systems may be very important in $\text{O}=\text{NOO}^-$ generation, stabilization, transformation to the isomeric nitrate (NO_3^-) form, or activation toward oxidation–nitration of substrates [12,13,19–24]. Whereas iron [25] (e.g., heme) [12,26–30] and manganese [25,31–34] complexes have been studied with respect to bio(chemical) $\text{O}=\text{NOO}^-$ -mediated chemistry (including as decomposition catalysts [14,35]), studies of copper peroxyxynitrite chemistry are rather limited [10,34,36–45]; There are a few examples of kinetic studies of peroxyxynitrite interactions with copper salts, and one example of a copper complex effecting $\text{O}=\text{NOO}^-$ decomposition. However, we also recently reported some preliminary chemistry where a cupric superoxide complex $[(\text{TMG}_3\text{tren})\text{Cu}^{\text{II}}(\text{O}_2^-)]^+$ [TMG₃tren is tris(2-(*N*-tetramethylguanidyl)ethyl)amine] reacts with $\cdot\text{NO}_{(\text{g})}$ to give a discrete peroxyxynitrite species $[(\text{TMG}_3\text{tren})\text{Cu}^{\text{II}}(\text{O}=\text{NOO}^-)]^+$, the first example of such a species [45].

Here, key advances are described within a somewhat complementary chemical system:

1. A new peroxyxynitrite complex, $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$ (see later), employs a tridentate and not a tetradentate ligand.
2. In this new example, the synthesis instead begins with a copper–nitrosyl complex [2,46–48], which is then exposed to O_2 .
3. Density functional theory (DFT) calculations reveal that the nitrogen monoxide must dissociate from the Cu–NO moiety prior to $\text{Cu}^{\text{I}}/\text{O}_2$ reaction and peroxyxynitrite formation.
4. The new $\text{Cu}^{\text{II}}(\text{O}=\text{NOO}^-)$ species thermally transforms to a copper(II)–nitrito complex with evolution of O_2 . We observed this before with the thermal transformation of $[(\text{TMG}_3\text{tren})\text{Cu}^{\text{II}}(\text{O}=\text{NOO}^-)]^+$; yet this is another rather unusual case since most often peroxyxynitrite interacts with metal ions, leading to its isomerization to nitrate or effecting a substrate nitration.
5. We present the first demonstration of exogenous substrate oxidative reactivity directly from the new peroxyxynitrite–metal complex.

Points 1 and 2 portend to a future broad scope for $\text{Cu}/\text{O}_2/(\cdot\text{NO})$ chemistry. Together, the results point to the viability of biological $\text{Cu}/(\cdot\text{NO})/(\text{O}_2)$ peroxyxynitrite formation, i.e., not coming from free superoxide plus $\cdot\text{NO}_{(\text{g})}$ reaction (vide supra). Such a process may already have been observed for Cu,Zn superoxide dismutase [22–24] and cytochrome *c* oxidase [19].

Results and discussion

When purified $\cdot\text{NO}_{(\text{g})}$ is bubbled into a solution of $[\text{Cu}^{\text{I}}(\text{AN})]^+$ [AN is 3,3'-iminobis(*N,N'*-dimethylpropylamine)] in CH_2Cl_2 or tetrahydrofuran (THF) at -80°C , a nitrosyl complex formulated as $[\text{Cu}^{\text{I}}(\text{AN})(\text{NO})]^+$ is produced (Fig. 1; $\lambda_{\text{max}} = 264, 284, 346 \text{ nm}$, Fig. 2a¹; $\nu_{\text{NO}} = 1,736 \text{ cm}^{-1}$) (see the electronic supplementary material).

¹A weak 655 nm absorption observed is believed to be from a dimer form with bridging NO ligands, $\text{Cu}_2^{\text{II}} - (\text{NO}^-)_2$; further investigations are required.

$[\text{Cu}(\text{AN})(\text{NO})]^+$, a $\{\text{CuNO}\}^{11}$ species [2,49,50], would typically be thought of as a $\text{Cu}^{\text{II}}-(\text{NO}^-)$ complex; however, recent experimental and theoretical considerations are instead consistent with a $\text{Cu}^{\text{I}}-(\cdot\text{NO})$ electronic structural description [4,51,52]. Present DFT calculations at the B3LYP level of theory (see “Materials and methods”) show a spin density of 0.05 and -1.02 for the $[\text{Cu}^{\text{I}}(\text{AN})(\text{NO})]^+$ copper and NO fragments, respectively, also strongly supporting this electronic description (Table 1).² The binding energy of $\cdot\text{NO}$ and $[\text{Cu}^{\text{I}}(\text{AN})]^+$ is calculated to be exothermic by $3.3 \text{ kcal mol}^{-1}$. Consistent with the above description of $[\text{Cu}^{\text{I}}(\text{AN})(\cdot\text{NO})]^+$, its EPR spectrum (Fig. 2b) is not that typical of copper(II) complexes, but rather it possesses a relatively broad $g \sim 2$ resonance (however, lacking the hyperfine structure seen elsewhere) [4,48,51].

With excess $\text{NO}_{(\text{g})}$ removed, bubbling O_2 through the solution of $[\text{Cu}^{\text{I}}(\text{AN})(\text{NO})]^+$ (-80°C) leads to a light to deep blue color change as the peroxynitrite complex formulated as $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$ [$\lambda_{\text{max}} = 258, 294, 377(\text{s}), 681 \text{ nm}$, Fig. 2a] is formed. Its EPR spectrum (Fig. 2c) is typical of a tetragonal copper(II) complex, i.e., with a $d_{x^2-y^2}$ ground state. $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$ possesses only moderate solution stability (i.e., for several or more minutes, based on the UV-vis criterion), thus far preventing characterization by X-ray diffraction or resonance Raman spectroscopy.

X-ray structures are not known for peroxynitrite-metal species. Wick et al. [53] isolated (as a solid) the compound $[(\text{NC})_5\text{Co}(\text{OON}=\text{O})]^{3-}$, where $\kappa^1\text{-O-OON}=\text{O}$ binding was suggested. However, on the basis of DFT calculations, Videla et al. [54] proposed N-ligation for a peroxynitrite complex formulated as $[\text{Fe}(\text{CN})_5(\text{ONOO}^-)]^{3-}$ [54]. For metalloporphyrins, both N- and O-bound forms have been discussed [13,28,55].

Using DFT calculations (see footnote 2), we have explored different possible binding structures of the peroxynitrite ligand to the $[\text{Cu}^{\text{II}}(\text{AN})]^{2+}$ moiety. The structure shown in Fig. 3 was found to be the lowest-energy structure for $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$, featuring a cyclic bidentate $\kappa^2\text{-O,O'-OON}=\text{O}$ peroxynitrite ligand bound to the copper ion, with one short, $1.916\text{\AA}$, and one long, $2.314\text{\AA}$, Cu-O distance (Table 2). This is 4 kcal mol^{-1} more stable than another $\kappa^2\text{-O,O'-O}=\text{NOO}$ structure with similar Cu-O distances (Fig. 4a), or a $\kappa^1\text{-O-OON}=\text{O}$ -bound peroxynitrite (Fig. 4b). Our attempts to optimize a nitrogen-bound $\kappa^1\text{-N-O}=\text{NOO}$ peroxynitrite led to convergence to triplet O_2 and $[\text{Cu}^{\text{I}}(\text{AN})(\text{NO})]^+$ (Fig. 4c); thus, a Cu^{II} N-bound $\text{O}=\text{NOO}^-$ structure is unlikely. It is also of interest to consider how an N-bound nitrosyl might react with O_2 (as in $[\text{Cu}^{\text{I}}(\text{AN})(\text{NO})]^+ \rightarrow [\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$) to form a $\kappa^2\text{-O,O'-OON}=\text{O}$ peroxynitrite species. M-NO species may exist in O-bound states [56]; a side-on $\eta^2\text{-NO-Cu}$ moiety is known in nitrite reductase [48,57]. Such structures might facilitate attack by O_2 and (O)N-OO bond formation. However, $[\text{Cu}^{\text{I}}(\text{AN})(\text{NO})]^+$ is not calculated to react with O_2 (Fig. 4c).

Alternately, peroxynitrite (and subsequently nitrate) formation from nitrosyl-myoglobin or nitrosyl-hemoglobin reaction with O_2 involves initial $\cdot\text{NO}_{(\text{g})}$ dissociation from iron followed by O_2 binding with the resulting Fe-O_2 moiety undergoing subsequent attack by $\cdot\text{NO}_{(\text{g})}$ [3,13,27]. Such a mechanism may also be operating here. Formation of $[\text{Cu}(\text{AN})(\text{O}_2)]^+$ by reaction of $[\text{Cu}(\text{AN})]^+$ and O_2 is endothermic by only $1.2 \text{ kcal mol}^{-1}$. Although not detected experimentally, the calculated $[\text{Cu}(\text{AN})(\text{O}_2)]^+$ complex (see the electronic supplementary material) would have some Cu^{II} superoxide character (the spin densities for the complex are

²As a general check of the validity of the calculations and the basis set employed in this report, they were repeated for the nitrito complex with known X-ray structure (described in this paper), $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]^+$, using two different (larger) basis sets. First, the calculations used a TZVP basis set for the copper atom. Then, an additional set of diffuse functions was added to nonmetal atoms. Although the three optimized structures are very similar to those obtained using the 6-311G* basis set, the latter provided closer agreement with the observed experimental X-ray structure (with its $d_{x^2-y^2}$ ground state). For these reasons, it was considered appropriate for use in the calculations and the results presented.

0.34 and 1.53 for Cu and O₂, respectively), and could react with $\cdot\text{NO}_{(\text{go})}$ to give $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$. The latter reaction, $[\text{Cu}^{\text{II}}(\text{AN})(\text{O}_2^-)]^+ + \text{NO} \rightarrow [\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$, is exothermic by 8.3 kcal mol⁻¹.

The subsequent reactivity of peroxynitrite complex $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$, i.e., its clean stoichiometric thermal transformation to a nitrito–copper(II) product and an oxidizing equivalent (Fig. 5), further strongly supports its formulation. If $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$ is allowed to warm to room temperature, the copper(II)–nitrito complex $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]^+$ forms in 70% isolated yield; its identity along with EPR (Fig. 2d) and UV–vis spectroscopic characteristics have been confirmed from an independent synthesis and X-ray structure determination (Fig. 5). The UV–vis spectra of nitrito complex $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]^+$ and peroxynitrite species $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$ (Fig. 2) are quite similar, but are in fact distinctive (e.g., *d–d* bands: $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$, $\lambda_{\text{max}} = 681 \text{ nm}$; $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]^+$, $\lambda_{\text{max}} = 700 \text{ nm}$). Their EPR spectra are also extremely similar (Fig. 2). These findings are not surprising: calculations were carried and the resultant lowest unoccupied molecular orbitals obtained (Fig. 6) for each complex show they possess a $d_{x^2-y^2}$ ground state, consistent with the observed nitrito–copper(II) $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]^+$ X-ray structure and EPR spectroscopic properties. As said, the EPR spectrum of $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$ is nearly identical to that of $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]^+$ (Fig. 2), as also expected on the basis of its ground state electronic structural similarity.

To be absolutely sure that we were not mistaking this nitrito–copper(II) complex $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]^+$ for a nitrate species such as $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_3^-)]^+$, the latter was independently synthesized and spectroscopically characterized (see “Materials and methods” and the electronic supplementary material). Its UV–vis and EPR spectra are similar but distinguishable, and to the eye each (pure) complex in solution or as a solid in fact appears clearly very different, green for $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]^+$ and blue for the nitrate complex.

In addition, 0.5 mol O_{2(g)} per Cu^{II}–(ONOO[−]) complex is evolved during the thermal transformation of peroxynitrite to the nitrite complex (Fig. 5). This was determined by sweeping the gases formed during the reaction into an alkaline pyrogallol test solution (see “Materials and methods” and the electronic supplementary material). Thus, our formulation of $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$ is very strongly supported by our isolation, identification, quantitation (i.e., high yields), and therefore accounting of the mass balance for the thermal transformation products of $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$, $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]^+ + \frac{1}{2}\text{O}_2$.

Such reaction scenarios, O₂ evolution and/or oxygenatom transfer, were previously suggested in an Fe–NO + O₂ reaction [58], and Clarkson and Basolo [59] first observed and quantitated the overall O₂ uptake for a cobalt–nitrosyl complex as being $\text{Co–NO} + \frac{1}{2}\text{O}_2 \rightarrow \text{Co–NO}_2^-$. As would be consistent with this reaction stoichiometry, perhaps a peroxynitrite complex formed (as was proposed) [59], and then this decayed to the observed nitrito–cobalt complex, giving back 0.5 mol equiv O₂. However, excepting the present case along with our recent report on $[(\text{TMG}_3\text{tren})\text{Cu}^{\text{II}}(\text{O=NOO}^-)]^+$ [45], direct spectroscopic evidence for a putative metal–peroxynitrite intermediate in a system undergoing transformation to nitrite (or nitrate) has not been previously described [3,58,60].

As noted above, thermal isomerization to a nitrate (NO₃[−]) complex is not observed in the present system, unlike what occurs for heme proteins. The process involving the transformation of $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$ to $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]^+$ plus O₂ merits further consideration and interrogation. The conversion of peroxynitrite or peroxynitrous acid (HOON=O) to nitrite and $\frac{1}{2}$ O₂ is known, the important mechanistic step being initial homolytic O–O cleavage [12,61,62].

The copper(II) ion mediated transformation of peroxyxynitrite anion to nitrite and O₂ in aqueous media has in fact been observed. A possible mechanism of reaction, as adapted here from that proposed by Babich and Gould [38] in a copper(II) plus peroxyxynitrite aqueous system, is as follows:

Note that from recent literature, computational analyses on a “cupryl” [copper(III)-oxo] entity suggest that its actual electronic structure is that of a copper(II)-oxyl (Cu^{II}-O·) triplet species [63,64], as we have depicted in the equations above. This species has yet to be observed in copper–oxygen chemistry [65]. Cu^{II}-O-O can otherwise be described as a copper(III)-peroxo (or hydroperoxo) species as was proposed and described by Babich and Gould [38]; a synthetic mononuclear copper(III)-peroxo complex is known [66]. However, depending on the ligand environment, this could or would be in equilibrium with copper(I) and O₂, as suggested would occur here. Clearly, further research is needed to understand the reactivity of these new peroxyxynitrite–copper(II) complexes.

Exhibiting peroxyxynitrite-like oxidative capability, [Cu^{II}(AN)(ONOO⁻)]⁺ effects exogenous phenol substrate oxidative coupling chemistry. When 2,4-di-*t*-butylphenol (2,4-DTBP) (2.5 equiv) is added to the –80 °C solution of [Cu^{II}(AN)(ONOO⁻)]⁺ and it is allowed to warm to room temperature, the typical oxidatively C–C coupled diphenol is formed in quite good yield (80%, based on the amount of [Cu^{II}(AN)(ONOO⁻)]⁺); a small amount of *ortho*-nitrated phenol could also be isolated (Fig. 7). Again, the copper product is the nitrito complex [Cu^{II}(AN)(NO₂⁻)]⁺, as identified by comparison with the authentic material. This contrasts with findings for copper–zinc superoxide dismutase and some chemical systems, where putative peroxyxynitrite complexes effect phenol nitration reactivity [39,67,68]. On the basis of known peroxyxynitrite or peroxyxynitrous acid chemistry [12,61,62], the coupling chemistry likely is initiated by phenol hydrogen-atom abstraction from a species derived from Cu^{II}–(ONOO⁻) O–O cleavage. However, this is a speculative suggestion, and future investigations on reaction mechanisms of copper ion peroxyxynitrite complexes will be required.

To provide further evidence that a peroxyxynitrite moiety is present in [Cu^{II}(AN)(ONOO⁻)]⁺, we added tetrabutylammonium chloride (tBu₄NCl) in fivefold excess, to displace the ONOO⁻ group with the very strong Cl⁻ ligand. An immediate color change occurs at –80 °C. The fact that a peroxyxynitrite group or species derived from it is (are) present is supported by the observation that added 2,4-DTBP is now primarily nitrated (Fig. 7). Thus, under the

solvent and reaction conditions employed, peroxyxynitrite copper(II) complex $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$ and free peroxyxynitrite react differently, but both in a manner consistent with our peroxyxynitrite formulation for $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$. Phenol (e.g., tyrosine) nitration is normally considered to occur via peroxyxynitrite homolytic O–O cleavage to give $\cdot\text{OH} + \cdot\text{NO}_2$; the former would abstract a phenolic hydrogen atom and the latter would then add to the resulting phenoxyl radical to give the nitrated product [69]. Some further experimental observations which highlight and distinguish the properties and identities of $[\text{Cu}^{\text{I}}(\text{AN})(\text{NO})]^+$, $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$, and $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]^+$ are summarized in the electronic supplementary material.

Conclusions

In summary, we have described here the formation, spectroscopic features, structure (based on DFT calculations) and reactivity of a discrete copper(II)–peroxyxynitrite complex $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$. While starting with a copper–nitrosyl complex $[\text{Cu}^{\text{I}}(\text{AN})(\text{NO})]^+$, DFT calculations suggest $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$ is formed via dissociation of $\cdot\text{NO}_{(\text{g})}$, reaction with $\text{O}_{2(\text{g})}$ and subsequent $\cdot\text{NO}_{(\text{g})}$ addition to a putative $[\text{Cu}-\text{O}_2^-]^+$ adduct. In solution, $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$ thermally transforms to a nitrito complex, $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]^+$ and O_2 , a process differing with that occurring for many other metal ion peroxyxynitrite mixtures where isomerization to nitrate instead occurs. Also, here for the first time we are able to describe initial reaction chemistry of a $\text{Cu}^{\text{II}}-(\text{O}=\text{NOO}^-)$ complex. It appears to directly oxidatively couple a phenol, while if peroxyxynitrite is forced off of the complex, it can effect nitration chemistry. Research to obtain further insights into this system and others is warranted, given the oxidative/nitrative capability of peroxyxynitrite, and the presence of copper ion in biological fluids or enzyme active sites which may facilitate $\text{Cu}/\text{O}_2/\cdot\text{NO}$ chemistry.

Materials and methods

All reagents and solvents were purchased from commercial sources and were of reagent quality. THF was distilled from sodium/benzophenone under argon; CH_2Cl_2 was purified over an activated alumina column. Research grade nitric oxide (from BOC Gases) was purified following the procedure of Ford and Lorkovic [3] by passage through a series of two KOH columns and distillation at -100°C . ^{15}NO (99% purity) was purchased from Icon (Summit, NJ, USA) and was received in a 25-mL breakseal flask (0.1% NO_2 contamination). Preparation and handling of air-sensitive compounds were performed under an argon atmosphere using standard Schlenk techniques or in an MBraun Labmaster 130 inert atmosphere (less than 1 ppm O_2 , less than 1 ppm H_2O) glove box filled with nitrogen. Deoxygenation of solvents was effected by bubbling argon through them for 30–45 min. UV–vis spectra were recorded with a Cary 50 Bio spectrophotometer equipped with a fiber-optic coupler (Varian) and a fiber-optic dip probe (Hellma; 661.302-QX-UV-2 mm). IR spectra were recorded with an ASI ReactIR™ 1000 Fourier transform IR reaction analyzer at ambient as well as low temperature. X-band EPR spectra were recorded with a Bruker EMX spectrometer with the sample temperature maintained at approximately -263°C using an Oxford Instruments ER 900 cryostat. All gas chromatography (GC)/mass spectrometry (MS) experiments were carried out and recorded using a Shimadzu GC-17A/GCMS0QP5050 gas chromatograph/mass spectrometer. All the GC experiments were carried out and recorded using a Hewlett-Packard 5890 Series II gas chromatograph. X-ray crystallography was performed at the Johns Hopkins University chemistry facility. A suitable single crystal of $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]\text{NO}_3^-$ (vide infra) was mounted in Paratone-N oil on the end of a glass fiber and transferred to the N_2 cold stream (-163°C) of an Oxford Diffraction Xcalibur3 system equipped with Enhance optics [$\text{Mo K}\alpha$ radiation ($\lambda = 0.71073\text{\AA}$)] and a CCD detector. The frames were integrated and a face-indexed absorption

correction and an interframe scaling correction were also applied with the Oxford Diffraction CrysAlisRED software package (CrysAlis CCD, Oxford Diffraction, version 1.171.27p5 beta). The structures were solved using direct methods and refined using the Bruker SHELXTL (version 6.1) software package (G.M. Sheldrick, 2000). Elemental analyses were performed by Desert Analytics (Tucson, AZ, USA) for air-sensitive samples. ^1H NMR spectra were recorded with a Bruker Avance 400 MHz Fourier transform NMR spectrometer at ambient temperature. Chemical shifts were referenced either to an internal standard (Me_4Si) or to residual solvent peaks. The starting material $[\text{Cu}^{\text{I}}(\text{AN})]\text{B}(\text{C}_6\text{F}_5)_4$ was synthesized according to a published procedure [70].

Generation of $[\text{Cu}^{\text{I}}(\text{AN})(\text{NO})]^+$ in THF

Bubbling of excess prepurified $\cdot\text{NO}_{(\text{g})}$ into a THF solution of $[\text{Cu}^{\text{I}}(\text{AN})]\text{B}(\text{C}_6\text{F}_5)_4$ (1.00 mM) with a three-way syringe connected to Schlenk line at $-80\text{ }^\circ\text{C}$ immediately affords the copper–nitrosyl complex, $[\text{Cu}^{\text{I}}(\text{AN})(\text{NO})]^+$ ($\lambda_{\text{max}} = 264, 284, 346, 655\text{ nm}$) (Figs. 1, 2a).

Generation of $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$ and $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]^+$ in THF

$[\text{Cu}^{\text{I}}(\text{AN})(\text{NO})]^+$ was generated in THF at $-80\text{ }^\circ\text{C}$ by bubbling an excess of prepurified $\text{NO}_{(\text{g})}$ through $[\text{Cu}^{\text{I}}(\text{AN})]\text{B}(\text{C}_6\text{F}_5)_4$ (1.2 mM solution) with a three-way syringe connected to Schlenk line. Excess $\text{NO}_{(\text{g})}$ was removed by several vacuum/argon purging cycles. Then, with use of a long syringe needle, $\text{O}_{2(\text{g})}$ was bubbled directly into the solution (5–10 s), leading to the formation of $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$ [$\lambda_{\text{max}} = 258, 294, 377(\text{s}), 681\text{ nm}$; $\epsilon = 520\text{ M}^{-1}\text{ cm}^{-1}$] (Fig. 2a), and its EPR spectrum was also recorded (Fig. 2c). Its thermal transformation to the nitrito complex, $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]^+$ [$\lambda_{\text{max}} = 262, 300, 380(\text{s}), 700\text{ nm}$; $\epsilon = 320\text{ M}^{-1}\text{ cm}^{-1}$], could be followed by UV–vis spectroscopy (Fig. 2a).

Isolation of $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]\text{B}(\text{C}_6\text{F}_5)_4$ via peroxynitrite complex formation

In a 50-mL Schlenk flask with added stirring bar, 100 mg (0.107 mmol) of $[\text{Cu}^{\text{I}}(\text{AN})]\text{B}(\text{C}_6\text{F}_5)_4$ was dissolved into 20 mL of dried and degassed THF under argon. This solution was then cooled to $-80\text{ }^\circ\text{C}$ using a dry ice/acetone bath. An excess of prepurified nitric oxide gas was bubbled in the cold solution and the solution was then allowed to stand for 5 min. From this solution the excess nitric oxide was removed by several vacuum/argon purging cycles and this was followed by bubbling an excess of oxygen in the solution, which afforded the corresponding copper–peroxynitrite intermediate. The excess oxygen was removed by several vacuum/argon cycles, then the solution was allowed to warm up to room temperature and was stirred for 2 h at this temperature. The volume of the solution was then reduced to 10 mL and 25 mL of pentane was added and the mixture was allowed to stand for several hours to afford the green–blue crystalline $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]^+$, which was then filtered through a coarse frit and dried under a vacuum. Yield: 75 mg (approximately 70%). Anal. Calcd for $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]\text{B}(\text{C}_6\text{F}_5)_4$ ($\text{C}_{34}\text{H}_{25}\text{BCuF}_{20}\text{N}_4\text{O}_3$): C, 41.84; H, 2.58; N, 5.74. Found: C, 41.45; H, 2.70; N, 5.59. IR (Nujol): 1,162, 1,187 cm^{-1} .

Generation of $[\text{Cu}^{\text{I}}(\text{AN})(\text{NO})]^+$, $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$, and $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]^+$ in 2-methyltetrahydrofuran, for EPR spectroscopy

In a glove box, 4 mg (4.3 μmol) $[\text{Cu}^{\text{I}}(\text{AN})]\text{B}(\text{C}_6\text{F}_5)_4$ was dissolved in 2 mL 2-methyltetrahydrofuran (solution concentration 2.1 mM) and 0.5 mL was equally distributed to three EPR tubes capped with rubber septa. The tubes were immersed in a $-94\text{ }^\circ\text{C}$ cold bath (liquid N_2 /hexane) and the copper–nitrosyl adduct $[\text{Cu}^{\text{I}}(\text{AN})(\text{NO})]^+$ was generated in all of the three EPR tubes by bubbling an excess of prepurified $\text{NO}_{(\text{g})}$ through the solution with a three-way syringe connected to the Schlenk line. The excess of $\text{NO}_{(\text{g})}$ was removed by several vacuum/argon purging cycles. One of the tubes was immediately frozen in liquid N_2 for EPR characterization. An excess of $\text{O}_{2(\text{g})}$ was bubbled through the other two

solutions using a long syringe needle. The immediate formation of the copper–peroxynitrite intermediate, $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$, occurred. Excess O_2 was removed by several vacuum/argon purging cycles, then a second EPR tube was frozen in liquid N_2 and the third was allowed to warm up to room temperature to generate the decomposition product $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]^+$ and was then frozen in liquid N_2 for EPR characterization (Fig. 2). $[\text{Cu}^{\text{I}}(\text{AN})(\text{NO})]^+$: $g = 1.99$. $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$: $g_{\perp} = 2.06$; $g_{\parallel} = 2.255$; $A_{\parallel} = 150 \times 10^{-4} \text{ cm}^{-1}$; $A_{\perp} = 34 \times 10^{-4} \text{ cm}^{-1}$. $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]^+$: $g_{\perp} = 2.06$; $g_{\parallel} = 2.258$; $A_{\parallel} = 150 \times 10^{-4} \text{ cm}^{-1}$; $A_{\perp} = 38 \times 10^{-4} \text{ cm}^{-1}$.

Synthesis of authentic $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]\text{B}(\text{C}_6\text{F}_5)_4$

The ligand AN (0.30 g, 1.6 mmol), CuCl_2 (0.22 g, 1.6 mmol), and AgNO_3 (0.48 g, 3.1 mmol) were dissolved in 20 mL CH_3CN and the solution was stirred for 20 min, whereupon a green solution developed with precipitation of gray solids. The cloudy solution was filtered through a Celite pad and to the clear filtrate was added 50 mL ether to precipitate a green solid, which was collected and dried under a vacuum to yield 0.54 g of $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)](\text{NO}_3^-)$ (95% yield). (The origin of the nitrate anion present is not clear; however, the preparation of this complex is reproducible). Calcd for $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)](\text{NO}_3^-)$ ($\text{C}_{10}\text{H}_{25}\text{CuN}_5\text{O}_5$): C, 33.47; H, 7.02; N, 19.51. Found: C, 33.41; H, 7.05; N, 19.10. X-ray-quality crystals of $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)](\text{NO}_3^-)$ were grown by adding Et_2O over a CH_3CN solution of the copper complex and allowing it to stand for several days at room temperature. $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)](\text{NO}_3^-)$ (0.12 g, 0.33 mmol) and $\text{KB}(\text{C}_6\text{F}_5)_4$ (0.24 g, 0.33 mmol) was dissolved in 15 mL CH_2Cl_2 and the solution was stirred for 30 min. Under reduced pressure, the CH_2Cl_2 was removed and then the remaining green residue was redissolved in 10 mL THF. The cloudy solution was passed through a medium frit to remove the insoluble off-white solid. Slow addition of heptane (50 mL) to the filtrate gave a green microcrystalline solid, which was washed with 50 mL of pentane and dried in vacuo to yield 0.25 g (78% yield). The product was recrystallized from CH_2Cl_2 /heptane, giving crystalline material. UV–vis (THF): $\lambda_{\text{max}} = 262, 300, 380$ (s), 700 nm ($\epsilon = 320 \text{ M}^{-1} \text{ cm}^{-1}$). Calcd for $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]\text{B}(\text{C}_6\text{F}_5)_4$ ($\text{C}_{34}\text{H}_{25}\text{BCuF}_{20}\text{N}_4\text{O}_2$): C, 41.84; H, 2.58; N, 5.74. Found: C, 41.82; H, 2.24; N, 5.62. An EPR spectrum of this complex is given in Fig. 8.

Synthesis of nitrate complex $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_3^-)]\text{B}(\text{C}_6\text{F}_5)_4$

$[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_3^-)]\text{B}(\text{C}_6\text{F}_5)_4$ and $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]\text{B}(\text{C}_6\text{F}_5)_4$ (vide supra) were synthesized to compare them with and identify the species obtained from the thermal decomposition of $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]\text{B}(\text{C}_6\text{F}_5)_4$. The ligand AN (0.30 g, 1.6 mmol) and $\text{Cu}^{\text{II}}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (0.37 g, 1.6 mmol) were dissolved in 20 mL THF and the solution was stirred for 20 min, whereupon a blue solution developed. Addition of excess pentane (60 mL) gave a blue precipitate. The clear liquid was decanted and the remaining solid was dried under a vacuum to yield 0.57 g of $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_3^-)](\text{NO}_3^-)$ (95% yield). Calcd for $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_3^-)](\text{NO}_3^-)$ ($\text{C}_{10}\text{H}_{25}\text{CuN}_5\text{O}_6$): C, 32.04; H, 6.72; N, 18.68. Found: C, 32.00; H, 6.62; N, 18.44. This $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_3^-)](\text{NO}_3^-)$ complex (0.13 g, 0.35 mmol) and $\text{KB}(\text{C}_6\text{F}_5)_4$ (0.24 g, 0.33 mmol) were dissolved in 2 mL THF, giving a dark blue solution. After 20 mL CH_2Cl_2 had been added and the resulting solution had been stirred for 30 min, the cloudy solution was filtered through a Celite pad. Slow addition of pentane (50 mL) to the filtrate gave a blue microcrystalline solid, which was washed with 50 mL of pentane and dried in vacuo to yield 0.25 g product (76% yield). UV–vis (THF): $\lambda_{\text{max}} = 262, 300, 700$ nm ($\epsilon = 390 \text{ M}^{-1} \text{ cm}^{-1}$). Calcd for $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_3^-)]\text{B}(\text{C}_6\text{F}_5)_4$ ($\text{C}_{34}\text{H}_{25}\text{BCuF}_{20}\text{N}_4\text{O}_3$): C, 41.17; H, 2.54; N, 5.65. Found: C, 40.90; H, 2.31; N, 5.57.

Reaction of $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$ with 2,4-DTBP

$[\text{Cu}^{\text{I}}(\text{AN})]\text{B}(\text{C}_6\text{F}_5)_4$ (25 mg (0.027 mmol)) was dissolved in 5 mL of degassed THF under argon in a 50-mL Schenk flask. $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$ was prepared as described earlier. A

solution of 2,4-DTBP (14 mg, 0.068 mmol) was prepared in 1 mL THF and 100 μ L and this was added to the peroxyxynitrite complex solution immediately after it had been generated. The solution was left for at -80°C for 2 h and then warmed to room temperature. The resulting reaction solution was stirred for 30 min and to it a saturated $\text{NH}_4\text{OH}/\text{H}_2\text{O}$ (15 mL) solution was added along with 10 mL CH_2Cl_2 . The mixture was stirred for 20 min and the CH_2Cl_2 layer was collected using a separatory funnel. The $\text{CH}_2\text{Cl}_2/\text{NH}_4\text{OH}/\text{H}_2\text{O}$ extraction was performed three times to ensure the complete extraction of copper ion into the aqueous phase. The collected CH_2Cl_2 solution was reduced in volume by rotary evaporation and analyzed by GC, GC/MS, and NMR spectroscopy. Commercially available authentic compounds were used for comparison, and calibration curves were constructed to calculate the yield of the products formed from the above-mentioned reactions (see the electronic supplementary material). The yields of nitrophenol and coupled biphenol products (see Fig. 7) were 5 and 80%, respectively.

Addition of tBu_4NCl to $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$ and substrate reactivity

$[\text{Cu}^{\text{I}}(\text{AN})]\text{B}(\text{C}_6\text{F}_5)_4$ (9 mg (9.980 μmol)) was dissolved in 7 mL of degassed THF in a Schenk tube. The peroxyxynitrite complex $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$ was prepared as described earlier. A precooled solution of tBu_4NCl (14 mg, 0.050 mmol) was prepared in 0.5 mL THF, and this was added to the peroxyxynitrite complex solution immediately after it had been generated. UV-vis changes occurred immediately after addition of 5 equiv tBu_4NCl to $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$, $\lambda_{\text{max}} = 256, 797 \text{ nm}$ (not shown). A solution of 2,4-DTBP (4.5 mg, 21.95 μmol) was prepared in 0.5 mL THF under argon and was added to the solution. The resulting mixture for left at -80°C for 30 min and then warmed to room temperature, after which it was stirred for 30 min and to it a saturated $\text{NH}_4\text{OH}/\text{H}_2\text{O}$ (15 mL) solution was added along with 10 mL CH_2Cl_2 . The resulting solution was stirred for 20 min and the CH_2Cl_2 layer was collected using a separatory funnel. The $\text{CH}_2\text{Cl}_2/\text{NH}_4\text{OH}/\text{H}_2\text{O}$ extraction was performed three times to ensure the complete extraction of copper. The collected CH_2Cl_2 was reduced in volume by rotary evaporation and was analyzed by GC and NMR (see "Materials and methods"). The yields of *o*-nitrophenol and the oxidatively coupled biphenol product were 55 and 12%, respectively.

Computational details

The geometries of all calculated complexes were computed within the DFT at the B3LYP level [71,72], using the 6-311G* basis set for copper, nitrogen, and oxygen atoms and the 6-31G* basis set for carbon and hydrogen. In all cases for the calculation of reaction energies, single-point calculations using the 6-311 G(2d,p) basis set were done on the previously optimized geometries. Solvent effects were taken into consideration using the polarized continuum model method with THF. All the optimized structures were characterized as real minima by diagonalization of the analytically computed Hessian ($\text{Nimag} = 0$). All the calculations were performed using the Gaussian 03 package [73]. The molecular orbital analysis was performed on the optimized structures using the AOMIX program [74,75]. The pictures of selected molecular orbitals were obtained using Molekel [76].

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Abbreviations

AN	3,3'-Iminobis(<i>N,N'</i> -dimethylpropylamine)
DFT	Density functional theory
2,4-DTBP	2,4-Di- <i>t</i> -butylphenol
tBu ₄ NCl	Tetrabutylammonium chloride
THF	Tetrahydrofuran
TMG ₃ tren	Tris(2-(<i>N</i> -tetramethylguanidyl)ethyl)amine

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Fig. 1. Generation of the copper–nitrosyl complex [Cu^I(AN)(NO)]⁺ [AN is 3,3'-iminobis(*N,N'*-dimethylpropylamine)] and its proposed structure. *THF* tetrahydrofuran

Fig. 2.

a UV-vis changes upon reaction of O_2 with $[\text{Cu}^{\text{I}}(\text{AN})(\text{NO})]^+$ (red) in tetrahydrofuran at -80°C giving $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$ (blue), which converts to $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]^+$ (black). EPR (X-band) spectra (2-methyltetrahydrofuran, approximately -263°C , 2 mM solutions) of **b** $[\text{Cu}^{\text{I}}(\text{AN})(\text{NO})]^+$, $g = 1.99$, **c** $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$, $g_{\parallel} = 2.255$, $A_{\parallel} = 150 \times 10^{-4} \text{ cm}^{-1}$, and **d** $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]^+$, $g_{\parallel} = 2.26$, $A_{\parallel} = 150 \times 10^{-4} \text{ cm}^{-1}$

Fig. 3.
Proposed structure for $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$; see text

Fig. 4. Optimized structures of $[\text{Cu}(\text{AN})(\kappa^2\text{-O-O'-ONOO}^-)]^+$ (a) and $[\text{Cu}(\text{AN})(\kappa^1\text{-O-OONO}^-)]^+$ (b), and the results of optimizing the $[\text{Cu}(\text{AN})(\text{N-ONOO}^-)]^+$ structure (c), from which O_2 dissociates, and which goes to the $[\text{Cu}^{\text{I}}(\text{AN})(\text{NO})]^+$ complex. Energy values are given relative to $[\text{Cu}(\text{AN})(\kappa^2\text{-O-O'-OONO}^-)]^+$ taken as a reference

Fig. 5.

Reactivity of the peroxynitrite complex $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^\cdot)]^+$, which gives the nitrito complex $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^\cdot)]^+$ while 0.5 mol equiv $\text{O}_{2(\text{g})}$ is liberated. Also shown is an ORTEP view of the X-ray structure of $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)](\text{NO}_3^-)$: Cu1–O1, 1.99 Å; Cu1–O2, 2.45 Å; Cu1–N1, 2.06 Å; Cu1–N2, 1.99 Å; Cu–N3, 2.07 Å; $\angle\text{O1–Cu1–O2} = 55.7^\circ$; $\angle\text{O1–N4–O2} = 114.6^\circ$; $\angle\text{N2–Cu1–N1} = 95.27^\circ$; $\angle\text{N2–Cu1–N3} = 94.43^\circ$; $\angle\text{N1–Cu1–N3} = 139.2^\circ$. Crystallographic data (CIF file) for the structure of $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)](\text{NO}_3^-)$ have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication no. CCDC-643374. Copies of the data can be obtained free of charge from the CCDC (12 Union Road, Cambridge CB2 1EZ, UK; Tel.: +44-1223-336408; Fax: +44-1223-336003; deposit@ccdc.cam.ac.uk; Web site: <http://www.ccdc.cam.ac.uk>)

Fig. 6.

Lowest unoccupied molecular orbitals of the nitrito complex $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]^+$ (*left*) and the peroxyxynitrite species $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$ (*right*), with Cu compositions of 59 and 56%, respectively. Both possess a $d_{x^2-y^2}$ ground state consistent with the observed X-ray structure and EPR spectrum of nitrito complex $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]^+$. A nearly identical EPR spectrum for the peroxyxynitrite complex $[\text{Cu}^{\text{II}}(\text{AN})(\text{ONOO}^-)]^+$ (Fig. 2) is thus expected

Fig. 7. Reactivity of the peroxynitrite complex $[Cu^{II}(AN)(ONOO^-)]^+$, which thermally transforms to the nitrito $[Cu^{II}(AN)(NO_2^-)]^+$ complex with liberation of 0.5 mol equiv O_2 . If a phenol is added, this substrate can be oxidatively coupled. Addition of chloride to $[Cu^{II}(AN)(ONOO^-)]^+$, meant to release peroxynitrite by ligand exchange, leads to exogenous phenol substrate nitration. Also, see the text

Fig. 8. EPR spectrum of authentic $[\text{Cu}^{\text{II}}(\text{AN})(\text{NO}_2^-)]^+\text{B}(\text{C}_6\text{F}_5)_4$ in 2-methyltetrahydrofuran (liquid helium, $-263\text{ }^\circ\text{C}$). $g_\perp = 2.04$; $g_\parallel = 2.25$; $A_\parallel = 150 \times 10^{-4}\text{ cm}^{-1}$

Table 1

Selected calculated bond distances, angles, natural population analysis (NPA) charges, and spin densities of $[\text{Cu}^{\text{I}}(\text{AN})(\text{NO})]^+$ [AN is 3,3'-iminobis(*N,N'*-dimethylpropylamine)]

Bond distances (Å)		Bond angles (°)	
Cu(1)–N(1)	1.918	Cu(1)–N(1)–O(1)	131.1
N(1)–O(1)	1.176	O(1)–N(1)–Cu(1)–N(4)	4.8
Cu(1)–N(2)	2.151		
Cu(1)–N(3)	2.083		
Cu(1)–N(4)	2.017		

	Charge	Spin density
Cu(1)	0.97	0.05
(NO)	–0.25	–1.02
(AN)	0.28	–0.03

Table 2

Selected bond distances, angles, NPA charges, and spin densities calculated for the species $[\text{Cu}(\text{AN})(\kappa^2\text{-O-O-OONO})]^+$

Bond distances (Å)			Bond angles (°)
Cu(1)–N(2)	2.042	N(2)–Cu(1)–O(1)	91.1
Cu(1)–N(3)	2.132	N(2)–Cu(1)–O(2)	161.6
Cu(1)–N(4)	2.133	Cu(1)–O(2)–O(3)	117.0
Cu(1)–O(2)	1.916		
O(3)–O(2)	1.414		
O(2)–N(1)	1.339	O(2)–O(3)–N(1)–O(1)	–4.6
N(1)–O(1)	1.210	Cu(1)–O(2)–O(3)–N(1)	21.3
O(1)–Cu	2.314	Cu(1)–O(1)–N(1)–O(3)	–10.8

	Charge	Spin density
Cu(1)	1.10	0.34
(OO–NO)	–0.39	1.53
(AN)	0.29	0.13