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A *trans*-Hyponitrite Intermediate in the Reductive Coupling and Deoxygenation of Nitric Oxide by a Tricopper–Lewis Acid Complex

Davide Lionetti, Graham de Ruiter, and Theodor Agapie*

Division of Chemistry and Chemical Engineering, California Institute of Technology, 1200 East California Boulevard, MC 127-72, Pasadena, California 91125, United States

Supporting Information

ABSTRACT: The reduction of nitric oxide (NO) to nitrous oxide (N_2O) is a process relevant to biological chemistry as well as to the abatement of certain environmental pollutants. One of the proposed key intermediates in NO reduction is hyponitrite ($N_2O_2^{2-}$), the product of reductive coupling of two NO molecules. We report the reductive coupling of NO by an yttrium–tricopper complex generating a *trans*-hyponitrite moiety supported by two μ-O-bimetallic (Y,Cu) cores, a previously unreported coordination mode. Reaction of the hyponitrite species with Brønsted acids leads to the generation of N_2O, demonstrating the viability of the hyponitrite complex as an intermediate in NO reduction to N_2O. The additional reducing equivalents stored in each tricopper unit are employed in a subsequent step for N_2O reduction to N_2, for an overall (partial) conversion of NO to N_2. The combination of Lewis acid and multiple redox active metals facilitates this four electron conversion via an isolable hyponitrite intermediate.

Nitric oxide (NO) has attracted much attention due to its relevance to biochemistry as well as environmental science.[1] Coupling of NO to form a N–N bond and generate N_2O and H_2O is a pivotal step in the anaerobic respiration cycle.[1b,2] Reduction of NO is also of interest for its potential to contribute to the abatement of NO_x pollutants.[3] In nature, one of the systems responsible for the reduction of NO to N_2O is the bacterial nitric oxide reductase (NOR) enzymes, which contain a heme/nonheme diiron active site.[1b,4] Evolutionarily related cytochrome *c* oxidases (C*c*Os) display a similar active site architecture (with Cu in place of the nonheme Fe) and can also catalyze the reduction of NO, albeit at lower efficiencies than O_2.[1b,e,5] A key step in the mechanism of NO reduction by these enzymes is the formation of a hyponitrite motif ($[N_2O_2]^{2-}$).[1e,6] Studies of NO reduction by heterogeneous catalysts have indicated that hyponitrite species are also relevant to their activity.[7]

The mechanism of the reduction of NO to N_2O has been probed in synthetic model systems based on the metals involved in biological NO reduction (Fe, Cu).[1c,e,8] Complexes of other transition metals have also been reported to display NO reduction activity.[1c,d,9] Despite these many investigations, only a handful of metal complexes that contain the hyponitrite motif have been reported, in which hyponitrite ligands adopt a variety of binding modes to metal centers (Figure 1).

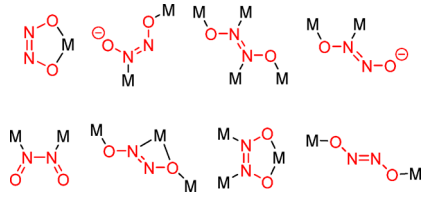

Figure 1. Binding modes of literature hyponitrite ligands.

Formation of hyponitrite from NO has been reported for Pt, Co, Ru, Ni, and Y compounds.[9−14] In some cases, treatment of hyponitrite complexes with H^+ sources results in the formation of N_2O.[1d,9c−f,10,14] A single hyponitrite complex featuring biologically relevant metals (based on the precedent of CcO and NOR) has been reported in which a *trans*-hyponitrite ligand bridges two Fe-porphyrin units.[6h,15] This complex also generates N_2O upon reaction with HCl. However, the hyponitrite ligand is obtained from hyponitrous acid rather than from reduction of NO.

We previously reported a series of $[MCu_3]$ complexes supported by a tripodal multinucleating ligand framework as models of the multicopper oxidases (Scheme 1).[16] $[Cu^I_3]$ complex **1** displays intramolecular metal cooperativity in reduction of O_2 at low temperature to a $[Cu^{III}Cu^{II}_2(\mu_3\text{-}O)_2]^{3+}$ intermediate. The pre-assembly of the three Cu centers in **1** was found to be essential to this reactivity, as related mononuclear or [YCu] complexes failed to generate the same intermediate. Herein, we describe the reactivity of **1** with NO to form a *trans*-hyponitrite complex, with subsequent reduction to N_2O and N_2.

To test for multimetallic reactivity with NO, a degassed propionitrile (EtCN) solution of **1** was exposed to gaseous NO (1.2 equiv) at −78 °C (Scheme 1). The solution was stirred for 6 h at −78 °C, after which it was allowed to warm to room temperature. Analysis by proton nuclear magnetic resonance spectroscopy (^{1}H NMR) of the yellow-green product indicates the disappearance of the sharp signals for **1** and the appearance of broad features, indicating formation of a paramagnetic species. Single crystal X-ray diffraction (XRD) analysis reveals a dimer of $[YCu_3]$ cores bridged by a *trans*-hyponitrite moiety resulting from reductive coupling of two NO molecules (**2**). At each $[YCu_3]$ unit, the oxygen atom from the $N_2O_2^{2-}$ ligand (O(13) and O(13′)) bridges between a Cu center and the Y center bound to the heptadentate site of the ligand framework

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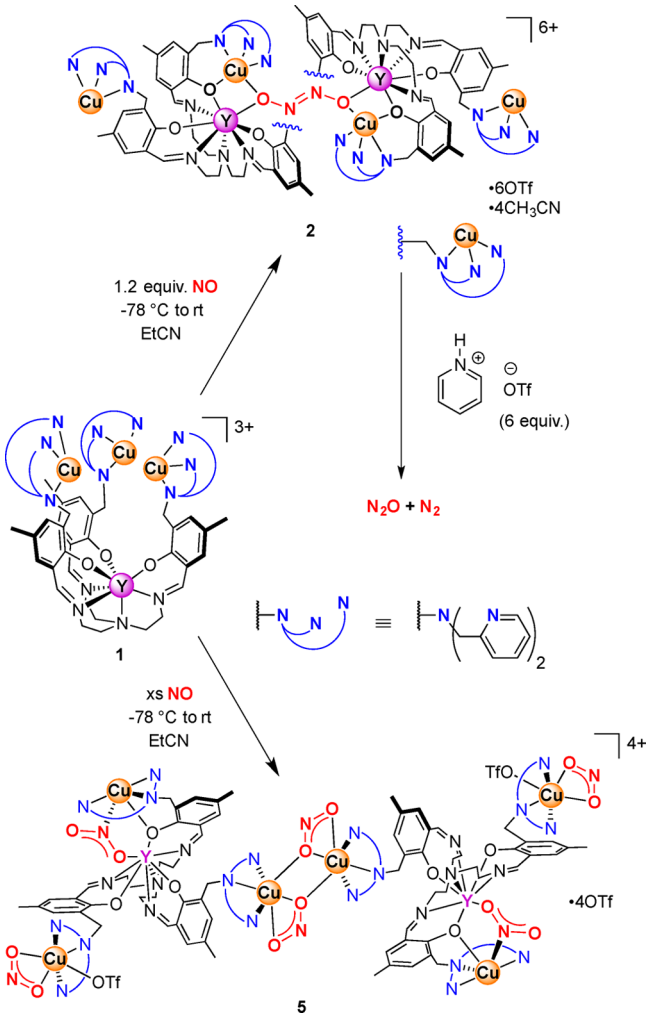
Scheme 1



(Figure 2), which represents a new binding mode for hyponitrite species. A second bridge between Cu and Y is provided by a phenoxide oxygen from the multinucleating ligand (O(1) and O(1′)). The hyponitrite-bound Cu center is five-coordinate and displays a square pyramidal geometry and was therefore assigned as Cu^{II}. The other two Cu centers remained essentially unchanged in their distorted tetrahedral geometries from the structure of the starting material **1**[16] and were assigned as Cu^{I}.

The overall reaction between **1** and NO corresponds to a 2-e^- reduction of two NO molecules by two Cu^{I} centers to give $N_2O_2^{2-}$ and two Cu^{II}. The Lewis acidic Y^{3+} center is key to this transformation as it provides an additional coordination site for stabilization of the hyponitrite ligand. Coordination of hyponitrite to Y^{3+} can be regarded as a Lewis acid/base analog to the Brønsted acid/base reaction with H^+ to ultimately generate N_2O in the natural system. While effects of Lewis acids on reduction of O_2 have previously been reported,[17] this is a rare demonstration of the effect of a Lewis acid on activation of NO. Notably, formation of **2** was the result of intermolecular activation of NO by two Cu and two Y centers, in contrast to the activation of O_2, which occurred intramolecularly.[16] Although the multinucleating ligand framework was shown to hold the three Cu centers in close proximity, thereby engendering cooperative O_2 activation, it is sufficiently flexible to allow coordination of an eighth ligand to Y^{3+}, important for the stabilization of the hyponitrite in **2**. Interestingly, the reduction of NO has been reported in a MOF displaying Fe and Lewis acid Zn^{2+} in close proximity, although a multinuclear reaction mechanism was not invoked.[18] Complex **2** is the first hyponitrite complex of a metal relevant to biological NO reduction (Cu as in CcO) in which the $N_2O_2^{2-}$ ligand is derived from nitric oxide.[1d]

The structural parameters for complex **2** were found to be very similar to those of literature *trans*-hyponitrite species. Both N−N and N−O bond distances in **2**, 1.254(8) and 1.376(4) Å, respectively, are within the ranges of values reported in the literature,[1c] consistent with an N−N double bond and N−O single bonds. Hyponitrite complexes have been reported to display characteristic bands in their infrared (IR) spectra corresponding to N−N and N−O stretching vibrations.[1c] However, due to the symmetric nature of **2** (an inversion center is present in the middle of the N(17)−N(17′) bond), the N−N (1400−1500 cm^{-1}) and symmetric N−O (900−1000 cm^{-1}) stretching vibrations are not expected to be IR active, akin to what was observed for an analogously symmetric porphyrin-supported Fe complex.[15] The IR-active asymmetric N−O stretch was observed at 980 cm^{-1} in the ATR-IR spectrum of **2** ($\nu(^{15}NO)$ = 970 cm^{-1}), similar to previously reported *trans*-hyponitrite complexes (Figure S4).

To gain insight into the role of the multimetallic nature of the precursor on the formation of **2**, the reactivity of monocopper complex **3** with NO was explored (Scheme 2). Treatment of **3** with NO (1 equiv) under analogous conditions to those used for **1** resulted in a change in color from yellow to

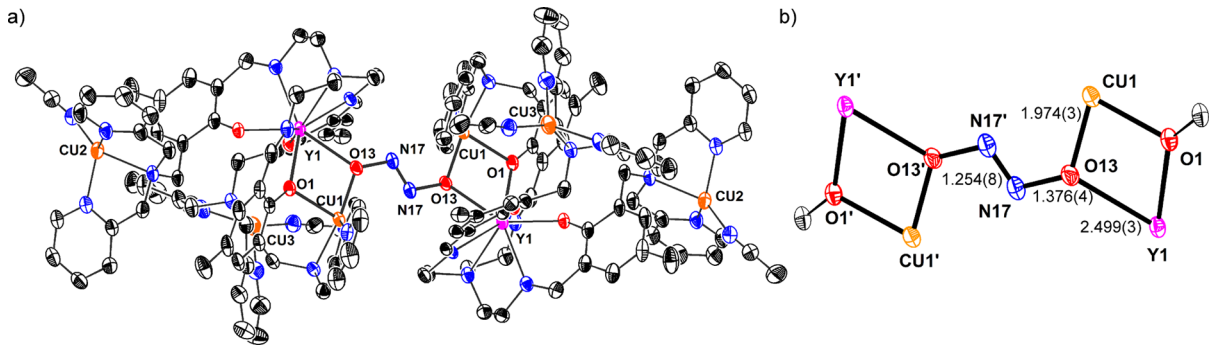


Figure 2. (a) Solid-state structure of the cationic portion of **2**. Hydrogen atoms, outer-sphere anions, and solvent molecules omitted for clarity. Thermal ellipsoids shown at the 50% probability level. (b) Cropped representation highlighting the hyponitrite motif in **2**, with relevant bond distances (in Å).

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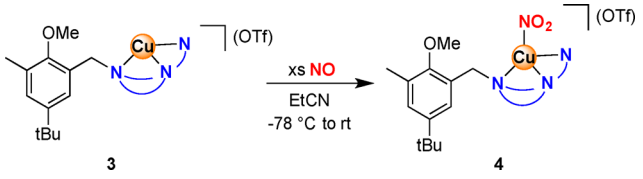
Scheme 2



dark green. Analysis by ^{1}H NMR reveals only partial conversion to a species with broad features (Figure S13). Complete conversion of **3** to a Cu^{II} nitrite (NO_2^-) complex, **4**, (Figure 3,

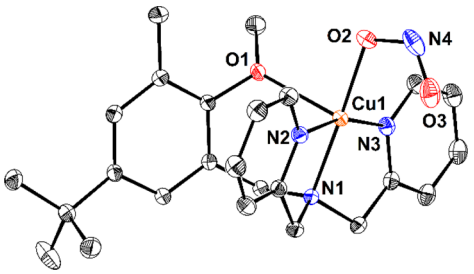


Figure 3. Solid-state structure of complex **4**. Hydrogen atoms and an outer-sphere triflate anion omitted for clarity. Thermal ellipsoids shown at the 50% probability level.

XRD) occurs only upon addition of excess NO (5 equiv). Observation of a nitrite complex and of a different stoichiometry suggests that treatment of **3** with NO results in reductive disproportionation to NO_2^-, supporting the notion that the presence of the Y^{3+} center in **1** is essential to stabilization of the bound hyponitrite moiety.

The reactivity of **1** with excess NO was investigated for comparison to **3**, and a similar outcome was observed (Scheme 1). One of the products of this reaction was characterized by XRD, and although the obtained data set was not of high enough quality for comparison of structural parameters, atom connectivity could be determined. The solid-state structure of complex **5** displays three NO_2^- ligands per [YCu_3] core (Figure S9), consistent with NO disproportionation reactivity of **1** in the presence of excess NO.

To determine whether hyponitrite complex **2** was a feasible intermediate in the reduction of NO to N_2O by **1**, its reactivity with Brønsted acids was explored. Complex **2** was found to react with pyridinium triflate, as observed by ^{1}H NMR. Addition of excess acid (up to ~5 equiv) led to complete consumption of starting material. To study the gaseous products of this reaction, after 3 h, N_2 was removed by freeze–pump–thaw cycles at −196 °C, and the remaining volatiles were vacuum-transferred to vessels cooled to −78 °C (to trap solvent CH_3CN) and −196 °C (to condense any produced N_2O). IR analysis of the product in a gas IR cell revealed formation of N_2O by comparison to an authentic sample (Figure S5), confirming the viability of **2** as an intermediate in the reduction of NO by **1**.

Given the presence of four Cu^{I} centers in **2**, potential for further *in situ* reduction of N_2O (to N_2) produced upon treatment with H^+ was hypothesized. Notably, N_2O reduction to N_2 is performed in nature by nitrous oxide reductase at a tetracopper active site, although the exact mechanism for this transformation is under debate.[19] Consistent with this hypothesis, complex **1** was found to react with N_2O to give (albeit more slowly) the same $[Cu^{III}Cu^{II}_2(\mu_3\text{-}O)_2]^{3+}$ intermediate obtained via reaction with O_2 (UV–vis, Figure S10). To explore the possibility of N_2 release from **2**, via N_2O, the reaction of ^{15}N-labeled **2** with pyridinium triflate under an Ar atmosphere was monitored by sampling the headspace and analyzing by gas chromatography mass-spectrometry. After 24 h, a peak at m/z = 46 for $^{15}N_2O$ was observed, consistent with the IR results. Beginning at 48 h, however, a peak at m/z = 30 appeared that was absent in blank experiments as well as at earlier reaction time points, consistent with the formation of $^{15}N_2$ (Figure S6). These results suggest that N_2O generated *in situ* can be further reduced by the remaining Cu^{I} centers. Complex **1** can therefore engage in NOR as well as nitrous oxide reductase activity, performing the overall four-electron reduction of two NO molecules to N_2. Although reduction of mononuclear Fe^{II} nitrosyl complexes by sulfite and bisulfite to generate N_2O and N_2 has been reported,[20] and heterogeneous catalysts for reduction of NO (including to N_2) have also been extensively studied,[3b] to our knowledge the present study is the first example of the two-step reduction of NO to N_2 by a discrete multimetallic complex without the need for an external reductant.

In summary, the reactivity of an yttrium–tricoppper complex with NO reveals coupling and deoxygenation chemistry. Reductive coupling of two NO molecules by two distinct [YCu_3] units results in formation of a *trans*-hyponitrite complex, **2**, in which each oxygen of the $N_2O_2^{2-}$ ligand bridges between Y and Cu centers. Binding of Lewis acidic Y^{3+} is proposed to stabilize the hyponitrite intermediate. Reaction of **2** with H^+ leads to the generation of N_2O. These results provide direct structural evidence for the intermediacy of hyponitrite species in the Cu-mediated reductive coupling of NO to N_2O relevant to biological systems. Additionally, reduction of N_2O generated *in situ* to N_2 was also observed, highlighting the ability of tricopper complex **1** to perform both NOR and nitrous oxide reductase activities. More broadly, the combination of Lewis acid and multiple redox active metals was demonstrated to facilitate four electron chemistry, involving coupling and deoxygenation of NO via a detectable hyponitrite intermediate.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b01083.

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Experimental details and data (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*agapie@caltech.edu

Notes

The authors declare no competing financial interest.

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