CHEMISTRY LETTERS, pp. 1521-1524, 1993.

Molecular Structure of Copper Nitrito Complex as the Reaction Intermediate of Dissimilatory Reduction of NO_2^-

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Electrochemical reduction of NO_2^- by $[Cu(tpa)(H_2O)](ClO_4)_2$ (tpa = tris[(2-pyridyl)methyl]amine) under the controlled potential electrolysis at -0.40 V (*vs.* Ag/AgCl) in H_2O (pH 7.0) catalytically produced N_2O with concomitant NO evolution. As the precursor of NO evolution, $[Cu(tpa)(ONO)]PF_6$ was characterized by X-ray crystallography.

Dissimilatory reduction (denitrification) of NO_2^- by nitrite reductases containing heme and copper proteins[1] is the key reaction of the nitrogen cycle, and has been widely investigated to elucidate the reaction mechanism.[2] There are, however, controversies about the precursors of NO and N_2O evolution in the pathway from NO_2^- to N_2O. We have demonstrated that $[Mo_2Fe_6S_8(SPh)_9]^{3-}$,[3] $[Fe_4S_4(SPh)_4]^{2-}$,[4] and $[MoFe_3S_4(SPh)_3(O_2C_6Cl_4)]_2^{4-}$ [5] catalyze the electrochemical reduction of NO_2^-, and the pathway of the reduction is largely influenced by the coordination mode of NO_2^- to those clusters (nitro and nitrito forms). Recently, a stoichiometric reaction of NO_2^- and NO with copper complexes has been studied in CH_2Cl_2 and EtCN.[6] Here, we report catalytic reduction of NO_2^- by a copper complex in H_2O (pH 7.0) and the molecular structure of a nitrito-Cu(II) complex as the precursor of NO evolution.

After an aqueous $NaNO_2$ (2 mmol) solution (10 cm^3) was mixed with an EtOH solution (25 cm^3) containing $(CH_3COO)_2Cu\cdot H_2O$ (1 mmol) and tris[(2-pyridyl)methyl]amine (tpa) (1 mmol), an addition of NH_4PF_6 (2 mmol) to the solution gave a green precipitate of a nitro adduct $[Cu(tpa)(NO_2)]PF_6$,[7] which exhibited the $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ bands at 1390 and 1330 cm^{-1} in the IR spectrum. Recrystallization of the nitro adduct from CH_3OH afforded single crystals of a nitrito adduct $[Cu(tpa)(ONO)]PF_6$ [8] showing ν(N=O) and ν(N-O) bands at 1426 and 1082 cm^{-1}. Both $[Cu(tpa)(ONO)]PF_6$ and $[Cu(tpa)(NO_2)]PF_6$ showed the same electronic absorption and IR spectra in acetonitrile,[9] suggesting that they exist as an equilibrium mixture in the solution (Eq. 1).

$$[Cu(tpa)(ONO)]^+ \rightleftharpoons [Cu(tpa)(NO_2)]^+ \qquad (1)$$

The molecular structure of $[Cu(tpa)(ONO)]PF_6$ (Fig. 1) is close to trigonal bipyramidal with the O1-Cu-N1 bond angle of 175.8(1)°.[10] The ONO moiety is located in the space formed by the Cu-N2, Cu-N3, and Cu-O1 bonds, and the Cu-N4 bond distance is longer than the other Cu-N bonds.

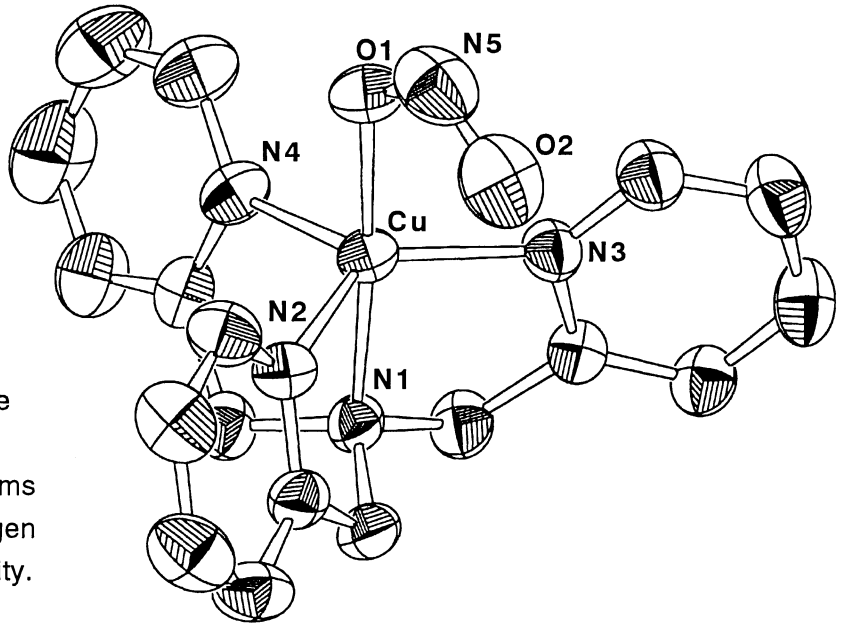

Fig. 1. Molecular structure of $[Cu(tpa)(ONO)]^+$ with atom labelling. Carbon atoms are not labeled and hydrogen atoms are ommited for clarity.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for $[Cu(tpa)(ONO)]PF_6$

Distances		Angles			
Cu-O1	1.938(2)	O1-Cu-N1	175.8(1)	N1-Cu-N4	81.1(1)
Cu-N1	2.031(2)	O1-Cu-N2	98.2(1)	N2-Cu-N3	131.3(1)
Cu-N2	2.026(2)	O1-Cu-N3	100.0(1)	N2-Cu-N4	113.2(1)
Cu-N3	2.047(2)	O1-Cu-N4	95.3(1)	N3-Cu-N4	109.6(1)
Cu-N4	2.129(2)	N1-Cu-N2	81.5(1)	Cu-O1-N5	118.0(2)
O1-N5	1.300(3)	N1-Cu-N3	83.2(1)	O1-N5-O2	114.8(3)
O2-N5	1.211(3)				

The cyclic voltammogram (CV) of $[Cu(tpa)(H_2O)](ClO_4)_2$ [11] shows the $[Cu(tpa)(H_2O)]^{2+/+}$ couple at E_{pc} = -0.47 and E_{pa} = -0.38 V with 0.10 V/s [12] in aqueous phosphate buffer solution at pH 7.0 (a solid line in Fig. 2).[13] An addition of $NaNO_2$ to the solution causes a catalytic current due to the copper-mediated reduction of NO_2^- at potentials more negative than -0.30 V (a dotted line in Fig. 2). In accordance with this, the controlled potential electrolysis of an aqueous solution (pH 7.0, 17 cm^3) [3 - 5, 14] containing $[Cu(tpa)(H_2O)](ClO_4)_2$ (14 μmol) and $NaNO_2$ (1.0 mmol) at -0.40 V (*vs.* Ag/AgCl) produced NO and N_2O (Fig. 3),[15] and the former becomes almost constant after 20 C. This observation strongly suggests that NO is the one of the reaction intermediate in the reduction of NO_2^- to N_2O. In fact, the controlled potential electrolysis of $[Cu(tpa)(H_2O)](ClO_4)_2$ in NO-saturated H_2O (pH 7.0) at -0.30 V[16] also produced N_2O,[17] as similar to the reduction of

NO to N_2O by a Cu nitrite reductase.[2d] Both $[Cu(tpa)(NO_2)]^+$ and $[Cu(tpa)(ONO)]^+$ formed by the reaction of $[Cu(tpa)(H_2O)]^{2+}$ with NO_2^- are considered to be the most possible intermediates in the reduction of NO_2^-. Removal of either terminal or Cu-bound oxygen from the Cu-O-N-O moiety upon the reduction of $[Cu(tpa)(ONO)]^+$ in H_2O would result in formation of unstable oxygen-bound nitrosyl complex, or dissociation of NO. The pathway from NO_2^- to NO, therefore, seems to be reasonably explained by the reduction of $[Cu(tpa)(ONO)]^+$ rather than $[Cu(tpa)(NO_2)]^+$, and a dimeric $(tpa)Cu^{II}\text{-}(NO^-)_2\text{-}Cu^{II}(tpa)$ has been proposed as the intermediate in a stoichiometric reduction of NO to N_2O by $[Cu^I(tpa)RCN]^+$.[6]

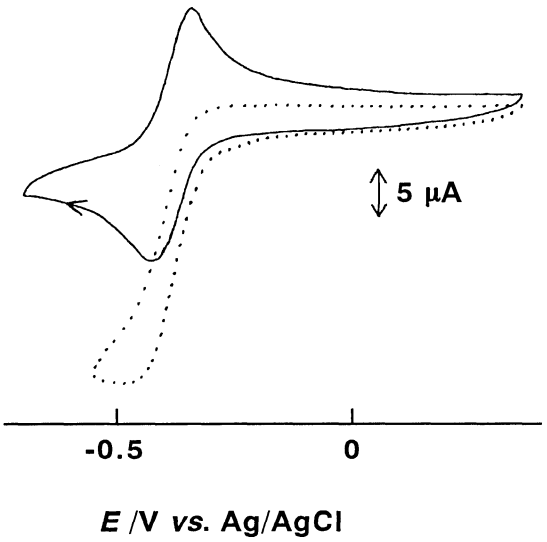

Fig. 2. Cyclic voltammograms of $[Cu(tpa)(H_2O)](ClO_4)_2$ (0.92 mmol dm^{-3}) in the absence (——) and the presence of $NaNO_2$ (2.8 mmol dm^{-3}; ·····) in H_2O at pH 7.0. ; $dE/dt = 0.10$ V/s.

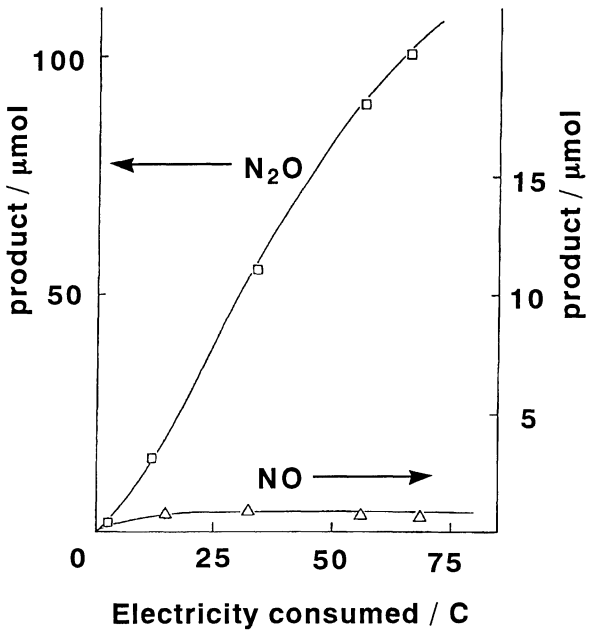

Fig. 3. Plots of the products *vs.* electricity consumed in the controlled potential electrolysis of $[Cu(tpa)(H_2O)](ClO_4)_2$ (14 μmol) and $NaNO_2$ (1.0 mmol) in H_2O (pH 7.0, 17 cm^3) at -0.40 V *vs.* Ag/AgCl.

This research was financially supported by Grant-in-Aid for Scientific Research on Priority Areas (No 03241106) from the Ministry of Education, Science and Culture.

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7) Yield 70%. Anal. Found: C, 39.73; H, 3.34; N, 12.87%. Calcd for $C_{18}H_{18}CuF_6N_5O_2P$: C, 39.68; H, 3.33; N, 12.85%.

8) Crystal data for [Cu(tpa)(ONO)]PF_6: $C_{18}H_{18}CuF_6N_5O_2P$, F. W. =544.88, monoclinic, space group $P2_1/a$, a=13.374(2) Å, b=14.033(2) Å, c=13.455(2) Å, β=119.10(1)°, V=2206.5(6) Å^3, Z=4, D_c=1.64 g cm^{-3}, R/R_w=0.039/0.022 for 3777 unique reflections (θ<30.0°) with $|F_o|>3\sigma(F_o)$ and 370 variables. The reflections were collected by θ–2θ scan technique on an Enraf-Nonius CAD4-GX21 automated four-circle diffractometer with MoKα radiation(0.7107 Å). All the calculation is carried out using a teXsan program.

9) Both [Cu(tpa)(NO_2)]PF_6 and [Cu(tpa)(ONO)]PF_6 showed the d-d transition band at λ_{max} = 838 nm (ε = 210) in CH_3CN, and the ν(N=O), $\nu_{as}(NO_2)$, and $\nu_s(NO_2)$ bands at 1426, 1387, and 1333 cm^{-1}, respectively, in CD_3CN. The ν(N-O) band of the nitrito complex was obscured by a strong absorption band of the solvent.

10) During this study, a molecular structure of [Cu($N(C_2H_4C_5H_4N)_3$)(ONO)]PF_6 was reported: F. Jiang, R. R. Contry, L. Bubacco, Z. Tyeklar, R. R. Jacobson, K. D. Karlin, and J. Peisach, *J. Am. Chem. Soc.,* **115**, 2093 (1993).

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12) The CV of [Cu(tpa)(H_2O)](ClO_4)$_2$ in H_2O (pH 7.0) showed at E_{pc} = -0.45 and E_{pa} = -0.39 V at 0.01 V/s.

13) The CV of [Cu(tpa)(ONO)]PF_6 is same as that of the mixture of [Cu(tpa)(H_2O)](ClO_4)$_2$ and $NaNO_2$ (1 : 1), and the dotted line of Fig. 2 is also identical to the CV of [Cu(tpa)(ONO)]PF_6 and $NaNO_2$ (1 : 2) in H_2O (pH 7.0).

14) pH was buffered with NaOH (1.0 mol dm^{-3})-H_3PO_4 .

15) Gas analysis was performed on a Shimadzu GC-8A gas chromatograph with molecular sieves 13X, and the details of the analysis are described in references 3, 4, and 5.

16) In the absence of [Cu(tpa)(H_2O)](ClO_4)$_2$, no detectable current flowed in the controlled potential electrolysis of aqueous $NaNO_2$ and NO-saturated H_2O (pH 7.0) at -0.40 V.

17) The current efficiency for the formation of gaseous N_2O was 60%.

(Received May 14, 1993)