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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 proteins1) 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 $\nu(N{=}O)$ and $\nu(N\text{-}O)$ 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.

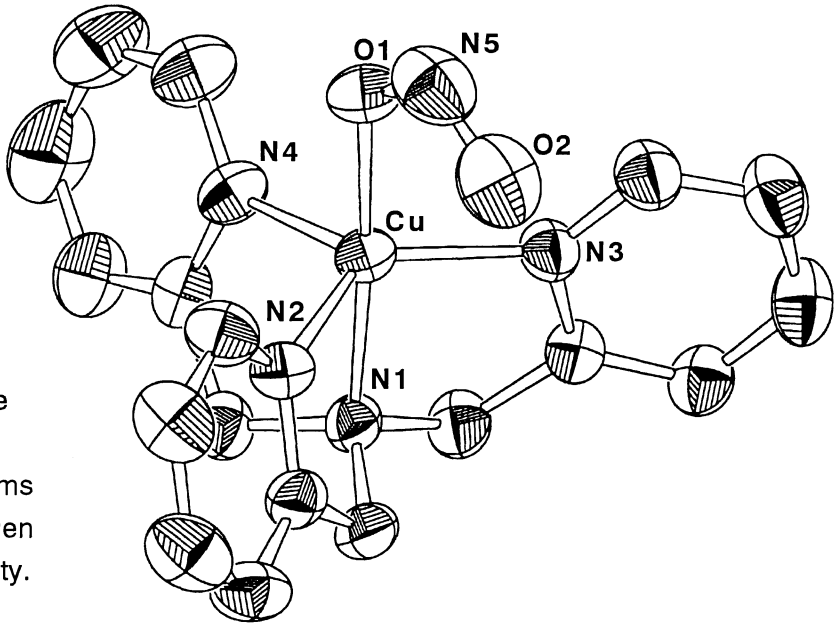

Fig. 1. Molecular structure of $[Cu(tpa)(ONO)]^+$ with atom labelling. Carbon atoms are not labeled and hydrogen atoms are ommited for clarity.

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 V16) 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]

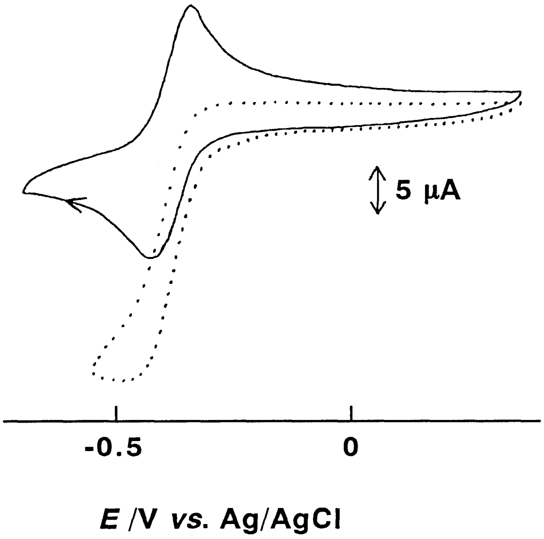

Fig. 2. Cyclic voltammograms of $[Cu(tpa)(H_2O)](ClO_4)_2$ (0.92 mmol dm^{-3}) in the absence (———) and the presence of $NaNO_2$ (2.8 mmol dm^{-3}; ········) in H_2O at pH 7.0. ; d*E*/d*t* = 0.10 V/s.

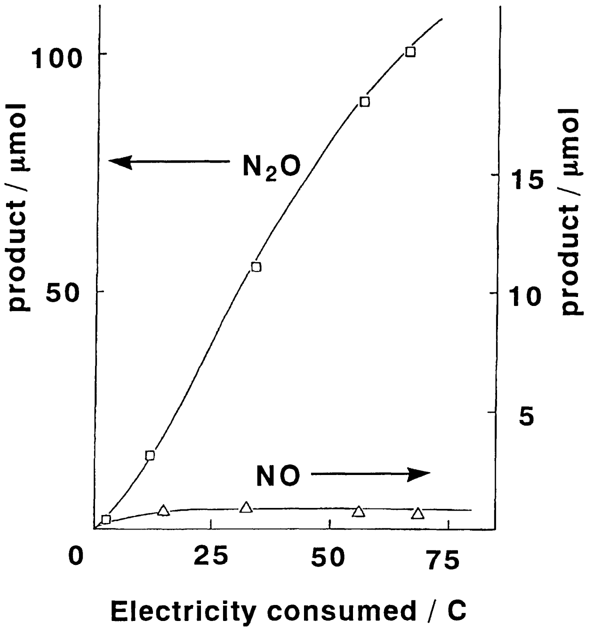

Fig. 3. Plots of the products *vs*. electricity consumed in the controlled potential electrolysis of $[Cu(tpa)(H_2O)](ClO_4)_2$ (14 μmol) and $NaNO_2$ (1.0 mmol) in H_2O (pH 7.0, 17 cm^3) at -0.40 V *vs*. Ag/AgCl.

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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 $\theta-2\theta$ 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%.

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