Molecular Structure of Nitro- and Nitrito-Copper Complexes as Reaction Intermediates in Electrochemical Reduction of Nitrite to Dinitrogen Oxide

Nobutoshi Komeda, Hirotaka Nagao,†† Yoshinori Kushi,†† Gin-ya Adachi,
Masatatsu Suzuki,† Akira Uehara,† and Koji Tanaka*,††

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565
†Department of Chemistry, Faculty of Science, Kanazawa University, Kakumamachi, Kanazawa 920-11
††Institute for Molecular Science, Department of Structural Molecular Science,
The Graduate University for Advanced Studies, Myodaiji, Okazaki 444

(Received July 7, 1994)

Copper-nitrito and -nitro isomers, [Cu(ONO)(tpa)]PF_6 and [Cu(NO_2)(tpa)]PF_6 (tpa=tris[(2-pyridyl)-methyl]amine) were isolated and the molecular structures were determined by X-ray analysis. [Cu-(ONO)(tpa)]PF_6 ($C_{18}H_{18}N_5O_2PF_6Cu$) crystallizes in the monoclinic space group $P2_1/a$ with $a=13.374(2)$, $b=14.033(2)$, $c=13.455(2)$ Å, $\beta=119.10(1)°$, $V=2206.5(6)$ Å^3, and $Z=4$. [Cu(NO_2)(tpa)]PF_6 ($C_{18}H_{18}N_5O_2PF_6Cu$) crystallizes in the orthorhombic space group $I/ba2$ with $a=16.718(3)$, $b=17.554(3)$, $c=14.785(3)$ Å, $V=4338(1)$ Å^3, and $Z=8$. Those nitrito- and nitro-complexes exist as an equilibrium mixture in solutions. Electrochemical reduction of NO_2^- in the presence of [Cu(H_2O)(tpa)](ClO_4)$_2$ at −0.4 V in H_2O (pH 7.0) catalytically produced N_2O with concomitant evolution of a small amount of NO via the nitro and nitrito adducts.

Nitrite ion coordinates to metal atoms in a variety of forms such as nitro, nitrito, chelating nitro, and bridging nitro.(1) Among those coordination modes, a nitro complex is reversibly converted to a nitrosyl complex by an acid–base equilibrium reaction. For example, [RuCl(NO_2)(bpy)$_2$] exists as an equilibrium mixture with [RuCl(NO_2H)(bpy)$_2$]$^+$ and [RuCl(NO)(bpy)$_2$]$^{2+}$ in H_2O.(2) A nitro-nitrosyl interconversion (E-NO_2^- and E-NO^+) is also proposed in enzymatic dissimilatory reduction of NO_2^-.(3—6) Both evolution of free NO and the N–N bond formation prior to N_2O evolution in the enzymatic reduction of NO_2^- have been ascribed to dissociation of nitrogen monoxide and an attack of the second NO_2^- (or NO) to E-NO^+ derived from E-NO_2^- via a dehydration reaction. These mechanistic hypotheses, however, are not fully accepted due to the lack of definitive evidence about each reaction step.

We have reported that coordination modes of NO_2^- (nitro and nitrito forms) to [$Mo_2Fe_6S_8(SPh)_9$]$^{3-}$,(7) [$Fe_4S_4(SPh)_4$]$^{2-}$,(8) and [$MoFe_3S_4(SPh)_3(O_2C_6Cl_4)$]$_2{}^{4-}$(9) crucially affect the pathways from NO_2^- to N_2O in the electrochemical reduction of NO_2^- by those clusters. The reductions of NO_2^- by copper and iron-porphyrin complexes are also of interest in connection with the reaction mechanisms of nitrite reductases containing copper and heme cd_1 proteins. Nitrite is shown to form a nitro adduct with iron-porphyrin complexes,(10) and the electrochemical reduction of NO_2^- by a water soluble iron-porphyrin affords NH_3, NH_2ON, and N_2O in H_2O.(4g) On the other hand, a nitrito copper complex has been obtained in a reaction of [CuCl(tepa)]$^+$ (tepa= tris[(2-pyridyl)ethyl]amine) with NO_2^-.(11) Catalytic behavior of a copper complex with nitrogen donors toward the reduction of NO_2^- is particularly relevant to copper-containing nitrite reductases, because the X-ray analysis of *Achromobacter cycloclastes* shows the presence of type I and type II copper sites with a distance of 12.5 Å as the possible electron mediator and the reaction center, respectively, and the type II copper is ligated with three histidines and water.(12)

This paper describes the reactions of [Cu(H_2O)-(tpa)]$^{2+}$ and [Cu(OH)(tpa)]$^+$ (tpa = tris[(2-pyridyl)-methyl]amine) with NO_2^-, and electrochemical reduction of NO_2^- to N_2O by [Cu(H_2O)(tpa)]$^{2+}$ through [Cu(ONO)(tpa)]$^+$ and [Cu(NO_2)(tpa)]$^+$ existing as an equilibrium mixture in H_2O. A part of this work have been reported elsewhere.(13)

Experimental

Physical Measurements. IR spectra were obtained on a Shimadzu FTIR-8100 spectrophotometer. Electrochemical measurements were performed in a Pyrex cell equipped with a glassy carbon working electrode, a Pt auxiliary electrode, an Ag/AgCl reference electrode, and a nozzle for bubbling of N_2. ESR spectra were obtained in frozen solutions at 77 K with 4-mm o.d. quartz tubes in a JEOL-JES-FE2XG ESR spectrometer operating at the X-band frequency. Electronic spectra were recorded on a Shimadzu UV-3100 instrument at room temperature. Cyclic voltammograms were obtained by use of a Hokuto Denko HAB-151 potentiostat/galvanostat with a function generator and a Riken Denshi F-35 X–Y recorder. FAB-Mass spectra were obtained on a Shimadzu/KRATOS CONCEPT 1S.

Materials. $(2\text{-}C_5H_4NCH_2)_3N$ (tpa),[14] $[Cu(H_2O)(tpa)](ClO_4)_2$,[15] $[Cu(CH_3CN)(tpa)]ClO_4$,[16] and $Na_2N_2O_2$[17] were prepared according to cited literature. Commercially available $Na^{15}NO_2$ (99.1 ATOM% ^{15}N) was purchased from Isotec Inc. and used without further purification.

$[Cu(NO_2)(tpa)]PF_6$. An addition of NH_4PF_6 (326 mg, 2.0 mmol) to a stirred H_2O/C_2H_5OH (2:5 v/v, 35 cm^3) solution containing $(CH_3COO)_2Cu{\cdot}H_2O$ (200 mg, 1.0 mmol), tpa (290 mg, 1.0 mmol), and $NaNO_2$ (138 mg, 2.0 mmol) afforded a green precipitate of $[Cu(NO_2)(tpa)]PF_6$. Recrystallization from H_2O gave $[Cu(NO_2)(tpa)]PF_6$ as green single crystals in the form of polyhedrons. Yield 70%. Anal. Calcd for $C_{18}H_{18}CuF_6N_5O_2P$: C, 39.68; H, 3.33; N, 12.85%. Found: C, 39.73; H, 3.34; N, 12.87%. IR spectrum (KBr) of $[Cu(NO_2)(tpa)]PF_6$, $\nu_{as}(NO_2)$ 1390 cm^{-1} and $\nu_s(NO_2)$ 1330 cm^{-1}. FAB-Mass spectrum: m/z 399 $(M-PF_6)$.

$[Cu(ONO)(tpa)]PF_6$. A hot CH_3OH solution of $[Cu(NO_2)(tpa)]PF_6$ gave green single crystals of $[Cu(ONO)(tpa)]PF_6$ on standing in a 70% yield. Anal. Calcd for $C_{18}H_{18}CuF_6N_5O_2P$: C, 39.68;H, 3.33; N, 12.85%. Found: C, 39.79; H, 3.38; N, 12.96%. IR spectrum (KBr) of $[Cu(ONO)(tpa)]PF_6$, ν(N=O) 1426 cm^{-1} and ν(N–O) 1082 cm^{-1}. FAB-Mass spectrum: m/z 399 $(M-PF_6)$.

Electrochemical Reduction of NO_2^- by $[Cu(H_2O)(tpa)](ClO_4)_2$ in H_2O. Reduction of $NaNO_2$ was carried out under controlled potential electrolysis conditions in an aqueous buffer solution at pH 7.0 (NaOH (1.0 $mol\,dm^{-3}$)–H_3PO_4) under He atmosphere. The cell consisted of three compartments; a glassy carbon working electrode (ϕ=3 mm), a Pt auxiliary electrode, and an Ag|AgCl reference electrode. The working and auxiliary compartments (17 and 12 cm^3, respectively) were separated with a Nafion® membrane. The working electrode cell was connected to a volumetric flask with a stainless tube. After a stream of He was passed through the electrolysis cell and the volumetric flask for 30 min to displace air, the reduction of $NaNO_2$ (1.0 mmol) in the absence and presence of $[Cu(H_2O)(tpa)](ClO_4)_2$ (14 μmol) in H_2O (17 cm^3) was started by applying the electrolysis potential to the glassy carbon plate electrode with a Hokuto Denko HA-501 potentiostat (−0.40 V vs. Ag|AgCl). The electricity consumed in the electrolysis was measured by a Hokuto Denko HF-201 coulometer. The electrochemical reduction of NO catalyzed by $[Cu(H_2O)(tpa)](ClO_4)_2$ (14 μmol) was conducted under the electrolysis −0.30 V after NO was bubbled into the solution for 30 min.

Product Analysis. At regular intervals, 0.1 cm^3 portions of gas in both the working electrode cell and the volumetric flask were sampled with a pressure-lock syringe (Precision Sampling) through septum caps attached to the tops of those compartments. Gas analysis was performed on a Shimadzu gas chromatograph GC-8A with a 2 m column filled with molecular sieves 13X at 313 K using He as a carrier gas. The mole ratios of $^{15}N^{15}NO$ to $^{14}N^{15}NO$ produced in the electrochemical reduction of $Na^{15}NO_2$ in the presence of $Na^{14}N_3$ were determined by a Shimadzu GC-Mass QP1000EX with a 2 m column filled with Unibeasds 1S. The analysis of the liquid phase was conducted by sampling 0.1 cm^3 portions of the solution in the working electrode cell with syringe techniques through the septum cap. After the solution was filtered with a membrane filter, the amount of NO_2^- in the filtrate was determined by an HPLC equipped with a conductometric detector (Toa Electronic Ltd. ICA-3030) and a 100 mm column packed with Toa Co., Ltd. PCI-201S at 313 K using an aqueous phthalic acid solution (2.5 $mmol\,dm^{-3}$) as an eluent (1.5 $cm^3\,min^{-1}$). A Shimadzu isotachophoretic analyzer, IP-2A, was used for analysis of *trans*-$HN_2O_2^-$ in the reaction mixtures by using $Cd(NO_3)_2$ (6.0 $mmol\,dm^{-3}$) and $CH_3(CH_2)_4COOH$ (10.0 $mmol\,dm^{-3}$) as leading and terminal electrolytes, respectively.

X-Ray Crystallographic Studies. Green prismatic crystals of $[Cu(NO_2)(tap)]PF_6$ and $[Cu(ONO)(tpa)]PF_6$ having approximate dimensions of 0.25×0.25×0.15 mm and 0.32×0.22×0.22 mm, respectively, were mounted on glass fiber with epoxy resin. The crystallographic data are summarized in Table 1. The reflections of X-ray analysis were collected by θ–2θ technique ($\theta<30°$) for $[Cu(ONO)(tpa)]PF_6$ and $[Cu(NO_2)(tpa)]PF_6$ on Enraf–Nonius CAD4-GX21 and Enraf–Nonius FR590 automated four-circle diffractometer with graphite monochromatized Mo $K\alpha$ radiation at 23 °C and −100 °C, respectively. All the calculations were carried out on an IRIS Indigo computer of Silicon Graphics corporation, using the TEXSAN crystallographic software package of Molecular Structure Corporation. The structure of $[Cu(ONO)(tpa)]PF_6$ was solved by heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically. Atomic scattering factors were taken from tables.[18] The final cycle of full-matrix least-squares refinements was based on 3777 observed reflections ($I>3.00\sigma(I)$) and 370 variable parameters. The structure of $[Cu(NO_2)(tpa)]PF_6$ was solved by direct methods and expanded Fourier techniques. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinements were based on 2426 observed reflections ($I>3.00\sigma(I)$) and 299 variable parameters. An empirical absorption correction using the program DIFABS[19] was applied; this resulted in transmission factors ranging from 0.73 to 1.29. The final atomic coordinates are listed in Tables 2 and 3.

Tables of atomic coordinates, thermal parameters, bond lengths, and angles for $[Cu(NO_2)(tpa)]PF_6$ and $[Cu(ONO)(tpa)]PF_6$ have been deposited as Document No. 68003 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Interconversion of Nitro and Nitrito Isomers. An addition of NH_4PF_6 to a 1:1:2 mixture of $(CH_3COO)_2Cu{\cdot}H_2O$, tpa, and $NaNO_2$ in H_2O/C_2H_5OH (2:5 v/v) resulted in precipitation of $[Cu(NO_2)(tpa)]PF_6$. Recrystallization of $[Cu(NO_2)(tpa)]PF_6$ from CH_3OH and H_2O selectively afforded

Table 1. Crystallographic Data for $[Cu(ONO)(tpa)]PF_6$ and $[Cu(NO_2)(tpa)]PF_6$

	$[Cu(NO_2)(tpa)]PF_6$	$[Cu(ONO)(tpa)]PF_6$
Chemical formula	$C_{18}H_{18}N_5CuF_6O_2P$	$C_{18}H_{18}N_5CuF_6O_2P$
a/Å	16.718(3)	13.374(2)
b/Å	17.554(3)	14.033(2)
c/Å	14.785(3)	13.455(2)
α/deg	90.00	90.00
β/deg	90.00	119.10(1)
γ/deg	90.00	90.00
V/Å^3	4338(1)	2206.5(6)
Z	8	4
Formula weight	544.88	544.88
Space group	$I/ba2$ (No. 45)	$P2_1/a$ (No. 14)
T/°C	−100	23
λ/Å	0.71069	0.71069
ρ_{calcd}/g cm^{-3}	1.67	1.64
μ/cm^{-1}	11.58	11.39
θ range/deg	<30.0	<30.0
Octants collected	$+h+k+l$	$\pm h+k+l$
No. of reflections measured	6722	6923
No. of data used ($I>3\sigma(I)$)	2426	3777
No. of variables	299	370
Final $R(F)/R_w(F)$/%	5.7/4.7	3.9/2.2

$R(F)=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. $R_w(F)=\{\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$.

single crystals of $[Cu(ONO)(tpa)]PF_6$ (ν(N=O) 1426 and ν(N−O) 1082 cm^{-1}) and $[Cu(NO_2)(tpa)]PF_6$ ($\nu_{as}(NO_2)$ 1390 and $\nu_s(NO_2)$ 1330 cm^{-1}), respectively (Fig. 1a). The selective crystallization of the nitro and nitrito adducts depending on the solvents indicates a smooth interconversion between the two complexes in solutions. In fact, a CD_3CN solution of $[Cu(NO_2)(tpa)]PF_6$ gives the same IR spectrum of $[Cu(ONO)(tpa)]PF_6$ in the same solvent, and the $\nu_{as}(NO_2)$, $\nu_s(NO_2)$, and ν(N=O) bands are observed at 1387, 1333, and 1426 cm^{-1}, respectively, in the solution (Fig. 1b).[20] Thus, $[Cu(NO_2)(tpa)]^+$ and $[Cu(ONO)(tpa)]^+$ exist as an equilibrium mixture in solutions (Eq. 1).

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

Molecular Structures of $[Cu(ONO)(tpa)]PF_6$ and $[Cu(NO_2)(tpa)]PF_6$. Three types of mononuclear Cu(II) nitrite complexes have been characterized so far; (i) binding to copper with one oxygen in $[Cu(ONO)(tepa)]PF_6$ (tepa=tris[2-(2-pyridyl)ethyl]amine)[11] and $[Cu(ONO)(OH_2)(terpy)]^+$,[21] (ii) binding through both oxygen atoms in $[Cu(NO_2)_2(bpy)]$[22] and $[Cu(NO_2)(bpy)_2]^+$,[23] (iii) coordination with nitrogen in $[Cu(NO_2)_6]^{4-}$,[24] and $K_3[Cu(NO_2)_5]$[25] involves all three binding modes. The molecular structures of the cationic portions for $[Cu(ONO)(tpa)]PF_6$ and $[Cu(NO_2)(tpa)]PF_6$ are depicted in Fig. 2, and the bond lengths and angles are collected in Table 4. The tpa ligands of both complexes coordinate to the Cu with the amino nitrogen atom (N1) and three pyridyl nitrogen atoms N(2—4).

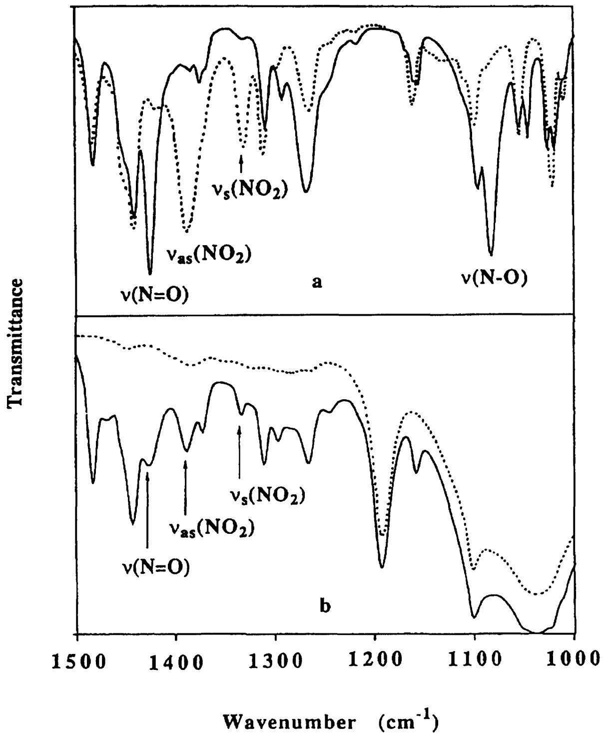


Fig. 1. (a) IR spectra of $[Cu(NO_2)(tpa)]PF_6$ (····) and $[Cu(ONO)(tpa)]PF_6$ (—) in KBr disks. (b) IR spectra in the absence (····) and presence (—) of $[Cu(ONO)(tpa)]PF_6$ in CD_3ON.

The nitrite ligand of $[Cu(ONO)(tpa)]PF_6$ is linked by one oxygen atom (O1) to Cu with the O1–N5–O2 bond angle of 114.8(3)°, similar to $[Cu(ONO)(tepa)]PF_6$ with

Table 2. Atomic Coordinates and B_{iso}/B_{eq} for [Cu(NO_2)(tpa)]PF_6

Atom	x	y	z	B_{eq}
Cu	0.24034(5)	0.24998(7)	0.1251	3.18(2)
P1	1.0000	0.0000	0.2220(2)	2.93(6)
P2	0.5000	0.0000	0.3435(3)	5.5(1)
F1	0.9092(2)	−0.0281(2)	0.2218(4)	4.2(1)
F2	0.9711(2)	0.0861(2)	0.2216(4)	4.0(1)
F3	1.0000	0.0000	0.3287(4)	4.4(2)
F4	1.0000	0.0000	0.1144(6)	5.3(2)
F5	0.4145(4)	0.0331(5)	0.3478(6)	11.0(3)
F6	0.5233(5)	0.0596(4)	0.4215(5)	9.4(3)
F7	0.5249(6)	0.0619(4)	0.2724(5)	12.3(3)
O1	0.3946(5)	0.2880(7)	0.0771(8)	10.1(3)
O2	0.3995(7)	0.2060(7)	0.148(1)	15.3(5)
N1	0.1194(3)	0.2483(4)	0.1185(5)	2.4(1)
N2	0.2290(4)	0.1808(4)	0.0122(5)	2.9(2)
N3	0.2200(3)	0.3645(3)	0.1131(5)	2.5(1)
N4	0.2153(5)	0.1960(4)	0.2483(5)	3.6(2)
N5	0.3558(4)	0.2521(6)	0.129(1)	5.8(2)
C1	0.0955(5)	0.1768(5)	0.0743(6)	3.3(2)
C2	0.1547(5)	0.1554(4)	0.0027(6)	3.0(2)
C3	0.1322(5)	0.1058(5)	−0.0682(6)	3.7(2)
C4	0.1906(7)	0.0843(5)	−0.1267(7)	4.6(2)
C5	0.2672(6)	0.1101(5)	−0.1193(8)	4.2(3)
C6	0.2829(6)	0.1588(5)	−0.0463(7)	3.7(2)
C7	0.0939(5)	0.3137(5)	0.0640(6)	3.0(2)
C8	0.1447(4)	0.3805(4)	0.0880(5)	2.6(2)
C9	0.1170(5)	0.4551(5)	0.0833(6)	4.0(2)
C10	0.1679(5)	0.5156(4)	0.1064(6)	3.8(2)
C11	0.2458(5)	0.4976(5)	0.1279(10)	3.6(1)
C12	0.2709(4)	0.4230(4)	0.1329(7)	3.1(2)
C13	0.0901(5)	0.2518(5)	0.2129(6)	3.6(2)
C14	0.1402(5)	0.2041(4)	0.2727(6)	3.1(2)
C15	0.1101(6)	0.1715(5)	0.3510(6)	4.6(2)
C16	0.1624(8)	0.1276(6)	0.4027(7)	5.5(3)
C17	0.2379(8)	0.1194(6)	0.3799(9)	5.2(3)
C18	0.2651(7)	0.1551(6)	0.2992(8)	5.1(3)

Table 3. Atomic Coordinates and B_{iso}/B_{eq} for [Cu(ONO)(tpa)]PF_6

Atom	x	y	z	B_{eq}
Cu	0.21095(3)	0.22112(2)	0.15624(3)	3.175(7)
P	0.86736(7)	0.39859(6)	0.60426(7)	3.97(2)
F1	0.7759(2)	0.3659(1)	0.4809(2)	7.56(6)
F2	0.9601(2)	0.4316(1)	0.7278(2)	7.08(6)
F3	0.7693(1)	0.4229(1)	0.6340(2)	6.57(6)
F4	0.9665(2)	0.3755(1)	0.5757(2)	6.55(6)
F5	0.8615(2)	0.5035(1)	0.5586(2)	7.00(6)
F6	0.8735(2)	0.2942(1)	0.6506(2)	7.52(6)
O1	0.0861(2)	0.3100(2)	0.1159(2)	4.40(5)
O2	0.1909(2)	0.4132(2)	0.0969(2)	6.19(7)
N1	0.3377(2)	0.1227(1)	0.2053(2)	3.02(5)
N2	0.3260(2)	0.2821(2)	0.3048(2)	3.26(5)
N3	0.2078(2)	0.2100(2)	0.0031(2)	3.41(5)
N4	0.1249(2)	0.1023(2)	0.1787(2)	3.77(6)
N5	0.1007(3)	0.3977(2)	0.0946(2)	5.68(8)
C1	0.4463(2)	0.1758(2)	0.2706(3)	3.72(8)
C2	0.4334(2)	0.2504(2)	0.3428(2)	3.33(7)
C3	0.5235(3)	0.2871(3)	0.4399(3)	4.61(8)
C4	0.5033(3)	0.3565(3)	0.4996(3)	5.46(10)
C5	0.3940(3)	0.3885(2)	0.4616(3)	4.97(9)
C6	0.3074(3)	0.3506(2)	0.3638(3)	4.11(8)
C7	0.3306(3)	0.0777(2)	0.1023(3)	3.75(8)
C8	0.2839(2)	0.1461(2)	0.0047(2)	3.16(7)
C9	0.3113(3)	0.1417(2)	−0.0813(3)	3.82(8)
C10	0.2573(3)	0.2021(3)	−0.1722(3)	4.93(10)
C11	0.1756(3)	0.2644(2)	−0.1768(3)	4.99(9)
C12	0.1548(3)	0.2672(2)	−0.0869(3)	4.18(8)
C13	0.3214(3)	0.0521(2)	0.2787(3)	3.64(8)
C14	0.1971(2)	0.0328(2)	0.2378(2)	3.60(7)
C15	0.1607(3)	−0.0502(2)	0.2657(3)	5.03(10)
C16	0.0470(4)	−0.0595(3)	0.2315(4)	7.1(1)
C17	−0.0292(4)	0.0116(3)	0.1712(4)	6.6(1)
C18	0.0129(3)	0.0914(3)	0.1450(3)	5.11(10)

the ONO bond angle of 114.9°. The O1–Cu–N1 bond angle for [Cu(ONO)(tpa)]PF_6 is 175.8(1)° and the remaining O1–Cu–N(2—4) bond angles are in the range of 95.3 to 100.0°. The structure of $[Cu(ONO)(tpa)]^+$ is, therefore, approximated by a trigonal bipyramid geometry. Although the terminal oxygen (O2) of the nitrito ligand is remote from the Cu (2.79 Å), the O2 oxygen may affect the equatorial Cu–N4 bond *trans* to the nitrito ligand since the distance of the Cu–N4 bond (2.129(2) Å) is longer than those of the Cu–N2 and Cu–N3 bonds (2.026(2) and 2.047(2) Å). A similar bond lengthening between Cu and pyridyl nitrogen *trans* to the nitrito group (2.253(5) Å) (distances between Cu and two nitrogen atoms are 2.039(5) and 2.049(5) Å) is observed in a distorted square pyramidal [Cu(ONO)(tepa)]PF_6.[11)]

The resolution of the two oxygen atoms (O1 and O2) of the nitro group in [Cu(NO_2)(tpa)]PF_6 is limited due to the disorder around the Cu–N5 bond (1.932(7) Å), but the remaining molecular structure is clear. The axial N5–Cu–N1 bond angle is 179.1(5)° and the N5–Cu–N(2—4) angles are 98—100°. In the equatorial plane, the N2–Cu–N3 and N2–Cu–N4 angles are almost the same (119.4(3) and 119.1(3)°), and the N3–Cu–N4 angle is 114.6(2). The structure of $[Cu(NO_2)(tpa)]^+$ is, therefore, also adequately approximated by a trigonal bipyramid geometry, similar to $[Cu(ONO)(tpa)]^+$. In addition, the Cu–N1 bond length for $[Cu(NO_2)(tpa)]^+$ (2.023(5) Å) is very close to that for $[Cu(ONO)(tpa)]^+$ (2.031(2) Å), suggesting that nitro and nitrito ligands gave a similar *trans* effect on the Cu–N1 bonds. The Cu–N5 bond distance of the nitro group (1.932(7) Å) for $[Cu(NO_2)(tpa)]^+$ is shorter than those of $[Cu(NO_2)_6]^{4-}$ (2.063—2.176 Å) and $K_3[Cu(NO_2)_5]$ (1.98—2.02 Å).

Redox Behavior of $[Cu(H_2O)(tpa)]^{2+}$ in CH_3CN. The cyclic voltammogram (CV) of [Cu(H_2O)(tpa)](ClO_4)$_2$ (1.2 mmol dm^{-3}) in CH_3CN shows the cathodic and anodic waves of the [Cu(H_2O)(tpa)]$^{2+/+}$ redox couple at $E_{pc}=+0.03$ and $E_{pa}=+0.10$ V (a solid line in Fig. 3). The redox couple at $E_{1/2}=+0.07$ V ($E_{1/2}=(E_{pc}+E_{pa})/2$) completely disappeared by an addition of more than 1.7 mmol dm^{-3}of NO_2^- to the solution and a new redox couple appears at

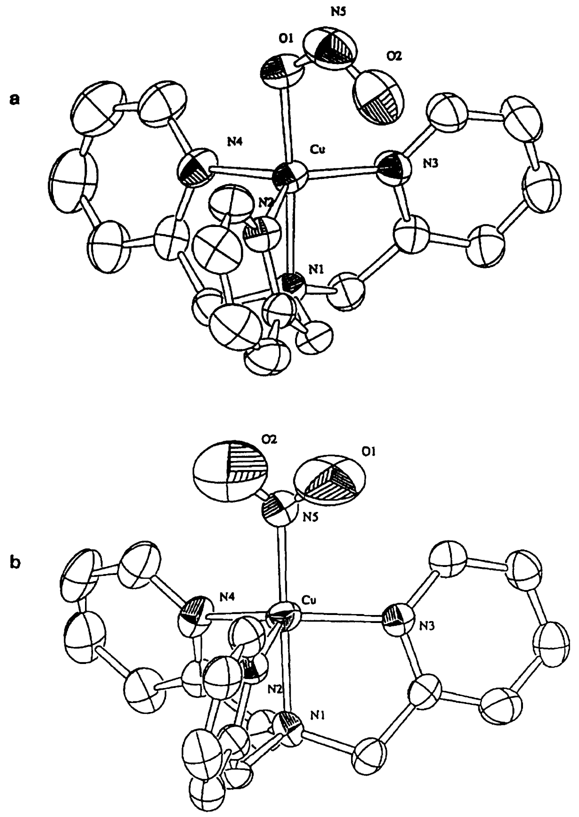


Fig. 2. Molecular structures of $[Cu(ONO)(tpa)]^+$ (a) and $[Cu(NO_2)(tpa)]^+$ (b) with atom labeling. Carbon atoms are not labeled and hydrogen atoms are omitted for clarity.

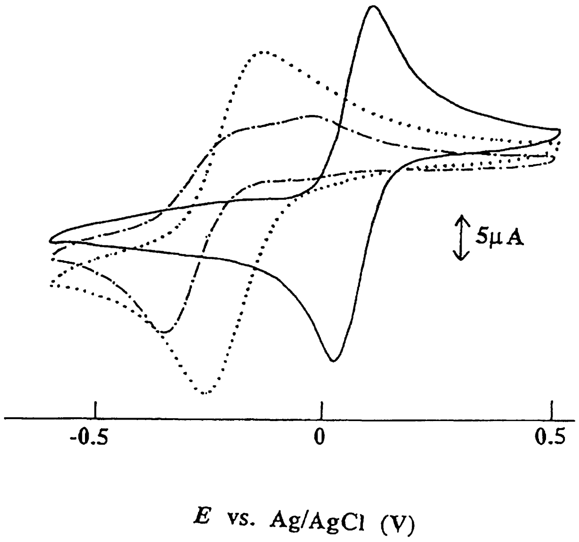


Fig. 3. Cyclic voltammograms of $[Cu(H_2O)(tpa)](ClO_4)_2$ (1.2 $mmol\,dm^{-3}$) in the absence (—) and presence of Bu_4NNO_2 (1.7 $mmol\,dm^{-3}$) at room temperature (····), and that in the presence of Bu_4NNO_2 in CH_3CN at −25 °C (–··–).

$E_{pc}=-0.26$ and $E_{pa}=-0.14$ V due to the adduct formation between $[Cu(H_2O)(tpa)]^{2+}$ and NO_2^- (a dotted line in Fig. 3). The emergence of the single redox couple at $E_{1/2}=-0.20$ V may be responsible for the first equilibrium reaction between $[Cu(ONO)(tpa)]^+$ and $[Cu(NO_2)(tpa)]^+$ in CH_3CN at 20 °C. In fact, the −0.26 V anodic wave at 20 °C is split into two waves ($E_{pa}=-0.20$ and −0.03 V) at −25 °C, although such a splitting is not observed at the cathodic wave ($E_{pc}=-0.35$ V) (a dotted dash line in Fig. 3).[26] According to assignments of redox potentials for $Ru^{II/III}$ couples of nitro and nitrito isomers,[27] the anodic waves at $E_{pa}=-0.20$ and −0.03 V observed at −25 °C in CH_3CN are tentatively assigned to the $[Cu(ONO)(tpa)]^{+/0}$ and $[Cu(NO_2)(tpa)]^{+/0}$ couples, respectively.

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for $[Cu(ONO)(tpa)]PF_6$ and $[Cu(NO_2)(tpa)]PF_6$

$[Cu(ONO)(tpa)]PF_6$		$[Cu(NO_2)(tpa)]PF_6$	
Distances (Å)			
Cu–O1	1.938(2)	Cu–N1	2.023(5)
Cu–N1	2.031(2)	Cu–N2	2.073(7)
Cu–N2	2.026(2)	Cu–N3	2.047(5)
Cu–N3	2.047(2)	Cu–N4	2.095(8)
Cu–N4	2.129(2)	Cu–N5	1.932(7)
O1–N5	1.300(3)	O1–N5	1.19(1)
O2–N5	1.211(3)	O2–N5	1.12(1)
Angles (deg)			
O1–Cu–N1	175.8(1)	N1–Cu–N2	82.0(3)
O1–Cu–N2	98.2(1)	N1–Cu–N3	81.1(2)
O1–Cu–N3	100.0(1)	N1–Cu–N4	80.6(3)
O1–Cu–N4	95.3(1)	N1–Cu–N5	179.1(5)
N1–Cu–N2	81.5(1)	N2–Cu–N3	119.4(3)
N1–Cu–N3	83.2(1)	N2–Cu–N4	114.6(2)
N1–Cu–N4	81.1(1)	N2–Cu–N5	97.5(5)
N2–Cu–N3	131.3(1)	N3–Cu–N4	119.1(3)
N2–Cu–N4	113.2(1)	N3–Cu–N5	98.6(3)
N3–Cu–N4	109.6(1)	N4–Cu–N5	100.3(5)
Cu–O1–N5	118.0(2)	Cu–N5–O1	122(1)
O1–N5–O2	114.8(3)	Cu–N5–O2	130(1)
		O1–N5–O2	101(1)

Interconversion between $[Cu(H_2O)(tpa)]^{2+}$ and $[Cu(OH)(tpa)])^+$ in H_2O. The electronic absorption spectrum of $[Cu(H_2O)(tpa)](ClO_4)_2$ shows an absorption band at 868 nm in H_2O at pH lower than 6.0. The absorbances at shorter and longer wavelength sides of the 868 nm band increase and decrease, respectively, with increasing pH of the aqueous solution, and an isosbestic point appears at 910 nm. Such a spectral change is reasonably explained by the equilibrium reaction between $[Cu(H_2O)(tpa)]^{2+}$ and $[Cu(OH)(tpa)]^+$ with the pK_a value of 7.4. (Eq. 2).[28] An addition of 10 molar excess of $NaNO_2$ to the aqueous solution of $[Cu(H_2O)(tpa)](ClO_4)_2$ (1.02 $mmol\,dm^{-3}$) at pH 6.0 resulted in the appearance of a new absorption band at 380 nm in the electronic absorption spectrum, which is essentially consistent with that of $[Cu(NO_2)(tpa)]PF_6$ in CH_3CN. On the other hand, the electronic spectrum of [Cu(OH)-

(tpa)]$^+$ at pH 10 was not changed even in the presence of 100 molar excess of $NaNO_2$. Thus, the aqua ligand of $[Cu(H_2O)(tpa)]^{2+}$ is easily substituted by NO_2^- to afford the equilibrium mixture of $[Cu(NO_2)(tpa)]^+$ and $[Cu(ONO)(tpa)]^+$ in H_2O, while the hydroxo ligand is inert for the substitution reaction. A stabilized copper–oxygen bond of $[Cu(OH)(Me_4tren)]^+$ resulting from a similar reversible dissociation of proton from $[Cu(OH_2)(Me_6tren)]^{2+}$ has been utilized to construct an asymmetric Cu^{II}–O–Fe^{III} bridge as a binuclear site model in oxidized cytochrome c oxidase.[29)]

$$[Cu(H_2O)(tpa)]^{2+} + OH^- \rightleftharpoons [Cu(OH)(tpa)]^+ + H_2O \quad (2)$$

Reversible conversion between $[Cu(H_2O)(tpa)]^{2+}$ and $[Cu(OH)(tpa)]^+$ in H_2O (Eq. 2) was detected also in the CV of $[Cu(H_2O)(tpa)](ClO_4)_2$ when Na_2SO_4 was used as a supporting electrolyte; a pair of cathodic and anodic waves of the $[Cu(H_2O)(tpa)]^{2+/+}$ couple were observed at $E_{pc}=-0.36$ and $E_{pa}=-0.30$ V at pH lower than 7. The $[Cu(OH)(tpa)]^{+/0}$ couple gradually emerged at $E_{pc}=-0.50$ V and $E_{pa}=-0.40$ V as the shoulders of the cathodic and anodic waves of the $[Cu(H_2O)(tpa)]^{2+/+}$ couple and pH higher than 7. The peak currents of the $[Cu(H_2O)(tpa)]^{2+/+}$ and $[Cu(OH)(tpa)]^{+/0}$ couples decreased and increased, respectively, with increasing pH, and the $[Cu(H_2O)(tpa)]^{2+/+}$ couple almost disappeared in the pH region above 9.

Reduction of NO_2^- by $[Cu(H_2O)(tpa)]^{2+}$ in H_2O. The redox waves of the $[Cu(OH)(tpa)]^{+/0}$ couple observed at pH above 9.0 are not much influenced by the presence of NO_2^- in the CV (Fig. 4). On the other hand, an addition of NO_2^- to the aqueous solution of $[Cu(H_2O)(tpa)]^{2+}$ (pH lower than 8.0) brings about a strong catalytic current due to the reduction of NO_2^- [30)] at potentials more negative than the threshold potential of the cathodic wave of the $[Cu(H_2O)(tpa)]^{2+/+}$ couple, then the anodic wave of the $[Cu(H_2O)(tpa)]^{2+/+}$ couple disappears. Thus, $[Cu(H_2O)(tpa)]^{2+}$ serves as an electrocatalyst in the reduction of NO_2^- at potentials more negative than -0.4 V in the pH region lower than 8, and the rate of the reduction increases with decreasing pH (Fig. 4). It is well know that nitrite ion spontaneously decomposes to NO and NO_3^- in strongly acidic water[31)] because of the lability of HNO_2 (pK_a=4.06[32)]) (Eq. 3).

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O \quad (3)$$

To avoid NO evolution by the spontaneous decomposition of NO_2^- in acidic conditions (Eq. 3), electrochemical reduction of NO_2^- by $[Cu(H_2O)(tpa)]^{2+}$ was carried out at pH 7.0. The controlled potential electrolysis of an aqueous solution (pH 7.0, 17 cm^3) containing $[Cu(H_2O)(tpa)](ClO_4)_2$ (14 µmol) and $NaNO_2$ (1.0 mmol) at -0.40 V (vs. Ag|AgCl) produced N_2O with the concomitant evolution of a small amount of NO.[33)] The amount of the latter became almost constant after 20 C (Fig. 5), while the former continuously increases dur-

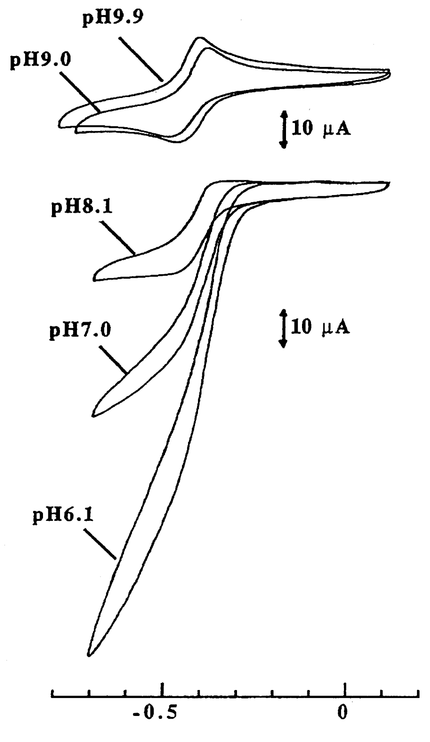


Fig. 4. Cyclic voltammograms of $[Cu(H_2O)(tpa)](ClO_4)_2$ (1.01 mmol dm^{-3}) in the presence of $NaNO_2$ (13.8 mmol dm^{-3}) in H_2O at various pH.

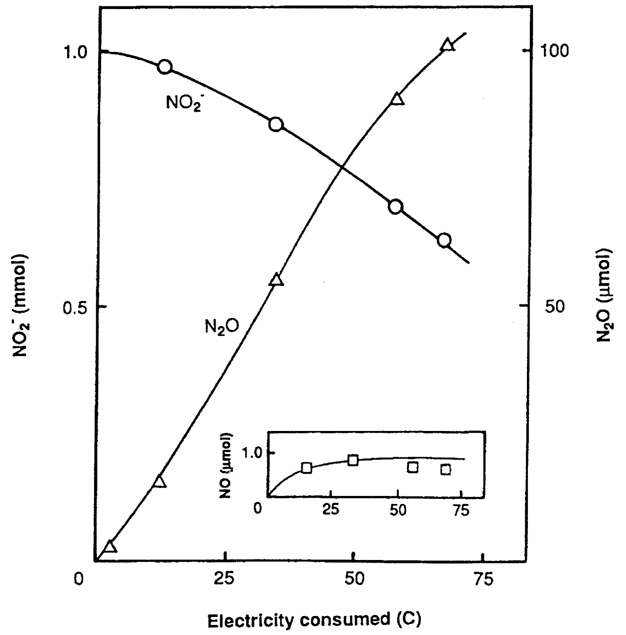


Fig. 5. Plots of amounts of N_2O and NO_2^- vs. electricity consumed under the controlled potential electrolysis of an aqueous solution (pH 7.0, 17 cm^3) containing $[Cu(H_2O)(tpa)](ClO_4)_2$ (14 µmol) and $NaNO_2$ (1.0 mmol) at -0.40 V vs. Ag/AgCl. Inset: Plots of the amount of NO vs. electricity consumed.

ing the electrolysis. The electronic absorption spectra of the electrolyte solution after 25 C passed in the electrolysis was essentially the same as that of the original solution (before the electrolysis). Thus, $[Cu(H_2O)(tpa)]^{2+}$ works stably as the electrocatalyst in the reduction of NO_2^- under the present reaction conditions. The reduction of $^{15}NO_2^-$ (1.0 mmol) in place of $^{14}NO_2^-$ by $[Cu(H_2O)(tpa)]^{2+}$ under the similar electrolysis conditions gave $^{15}N_2O$ with a current efficiency of 60% and neither $^{14}N_2O$ nor $^{15}N_2$ was detected by GC-Mass spectra. Furthermore, the controlled potential electrolysis of $[Cu(H_2O)(tpa)](ClO_4)_2$ in NO-saturated H_2O (pH 7.0) at −0.30 V (see below) also generated only N_2O with a current efficiency of 60%.[34] We, therefore, conclude that both NO_2^- and NO are smoothly reduced to N_2O electrochemically in the presence of $[Cu(H_2O)(tpa)]^{2+}$ in H_2O (pH 7.0).

Possible Pathways of NO_2^- Reduction of N_2O by $[Cu(H_2O)(tpa)]^{2+}$. In enzymatic reduction of $^{15}NO_2^-$, the presence of an E-$^{15}NO^+$ species is substantiated by evolution of $^{15}N^{14}NO$ in the presence of $^{14}N_3^-$ (Eq. 4). A similar $^{15}NO_2^-$ (25.7 mmol dm^{-3}) reduction by $[Cu(H_2O)(tpa)](ClO_4)_2$ (0.98 mmol dm^{-3}) in the presence of $Na^{14}N_3$ (1.0 mol dm^{-3}) under the electrolysis at −0.40 V in H_2O (pH 7.0) also produced a mixture of $^{14}N^{15}NO$ and $^{15}N_2O$ with a mole ratio of 1 : 0.63.[35] We have, however, found spontaneous $^{14}N^{15}NO$ and $^{14}N_2$ evolution from an aqueous solution (pH 7.0) containing $Na^{15}NO_2$ (93 mmol dm^{-3}) and $Na^{14}N_3$ (1.00 mol dm^{-3}) even in the absence of $[Cu(H_2O)(tpa)](ClO_4)_2$ (Eq. 5). In addition, the rate of $^{14}N^{15}NO$ evolution in the reaction of Eq. 5 was essentially the same as that in the electrochemical reduction of $^{15}NO_2^-$ by $[Cu(H_2O)(tpa)](ClO_4)_2$ in the presence of $^{14}N_3^-$ at −0.40 V in H_2O (pH 7.0). Thus, the spontaneous reaction of Eq. 5 does not give any evidence for the presence of Cu–NO$^+$ species in the reduction of NO_2^- by $[Cu(H_2O)(tpa)]^+$.

$$\text{E-}^{15}NO^+ + {}^{14}N_3^- \rightarrow E + {}^{14}N^{15}NO + {}^{14}N_2 \qquad (4)$$

$$^{15}NO_2^- + {}^{14}N_3^- + 2H^+ \rightarrow {}^{14}N^{15}NO + {}^{14}N_2 + H_2O \qquad (5)$$

The electrochemical reduction of NO_2^- by $[Cu(H_2O)(tpa)]^{2+}$ in H_2O produced N_2O with a small amount of NO, the latter of which is also reduced to N_2O under similar conditions. Furthermore, addition of $[Cu(CH_3CN)(tpa)]ClO_4$ to an NO-saturated aqueous solution (pH 7.0) gave rise to vigorous N_2O evolution; the reaction generated $[Cu(H_2O)(tpa)]^{2+}$ in an almost quantitative yield at room temperature. Electronic absorption spectra and ESR spectra of $[Cu(H_2O)(tpa)](ClO_4)_2$ did not show any interaction with NO in CH_3CN and H_2O. In accordance with this, treatment of Cu^I–NO with 2 mole of CH_3COOH affords NO and Cu^{II}-acetate complex.[36] On the other hand, the CV of $[Cu(H_2O)(tpa)](ClO_4)_2$ in an NO-saturated aqueous solution at pH 7.0 exhibits a strong irreversible cathodic wave at −0.34 V and the anodic wave of the $[Cu(H_2O)(tpa)]^{2+/+}$ couple at −0.37 V in the first potential sweep (Fig. 6).[37] The peak current of the −0.34 V cathodic wave decreases in the following potential sweeps and the −0.46 V cathodic wave of the $[Cu(H_2O)(tpa)]^{2+/+}$ couple clearly appears. The irreversible cathodic wave −0.34 V is associated with either positive potential shift of the $[Cu(H_2O)(tpa)]^{2+/+}$ couple caused by the succeeding rapid reaction of $[Cu(H_2O)(tpa)]^+$ with NO or direct reduction of NO in H_2O, since N_2O_2 equilibrated with NO undergoes the reduction at −0.40 V to afford *trans*-$H_2N_2O_2$($pK_1 = 7.0$ and $pK_2 = 11.0$)[38] in H_2O (pH 7.0).[39] The rate for N_2O evolution from an aqueous solution of $Na_2N_2O_2$ in the presence of $[Cu(H_2O)(tpa)](ClO_4)_2$ or $[Cu(H_2O)(tpa)](ClO_4)$ in H_2O (pH 7.0) at 25 °C, however, was negligibly slow compared with that in the electrochemical reduction of NO by $[Cu(H_2O)(tpa)](ClO_4)_2$ at −0.30 V. Furthermore, *trans*-$HN_2O_2^-$ was not detected at all during the electrolysis of NO_2^- by $[Cu(H_2O)(tpa)]^{2+}$. The −0.34 V cathodic wave (Fig. 6), therefore, may result from anodic potential shift of the $[Cu(H_2O)(tpa)]^{2+/+}$ couple. The emergence of the $[Cu(H_2O)(tpa)]^{2+/+}$ couple in the multi-scanning CV is explained by consumption of NO in the vicinity of the working electrode due to the reduction by $[Cu(H_2O)(tpa)]^+$.

The present electrochemical reduction of NO_2^- by $[Cu(H_2O)(tpa)]^{2+}$ possibly proceeds via $[Cu(ONO)(tpa)]^+$ and/or $[Cu(NO_2)(tpa)]^+$.[30] Reversible dehydration from $[Cu(NO_2)(tpa)]^+$ is reasonably ruled out, since there is no interaction between $[Cu(H_2O)(tpa)]^{2+}$ and NO in H_2O. Therefore, the most possible product is $[Cu(NO)(tpa)]^+$ through dehydration from nitro ligand. The almost quantitative evolution of N_2O in the reaction of $[Cu(CH_3CN)(tpa)]^+$ with NO may also pro-

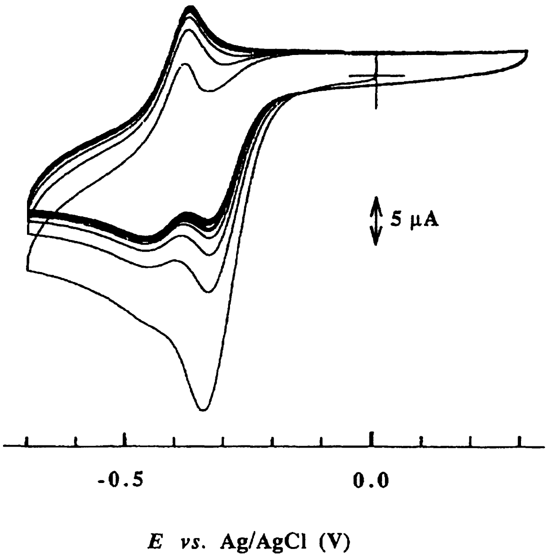
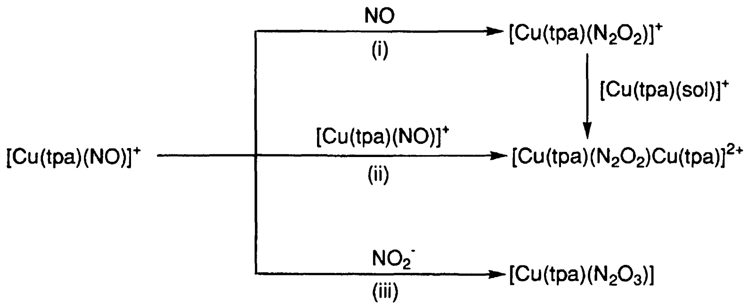


Fig. 6. Cyclic voltammograms of $[Cu(H_2O)(tpa)](ClO_4)_2$ (1.2 mmol dm^{-3}) in NO-saturated H_2O at pH 7.0; dE/dt 100 mV s^{-1}.



Scheme 1.

ceed via $[Cu(NO)(tpa)]^+$ as a reactive intermediate. It is, however, not clear whether $[Cu(NO)(tpa)]^+$ resulting from the electrochemical reduction of $[Cu(NO_2)(tpa)]^{2+}$ in H_2O dissociates NO or not prior to the subsequent evolution of N_2O, since a monomeric nitrosyl-copper complex, $[Cu(NO)(HB(t\text{-}Bupz)_3)]$ (pz=pyrazolate) isolated in a reaction of $[Cu(HB(t\text{-}Bupz)_3)]_2$ or $[Cu(CH_3CN)(HB(t\text{-}Bupz)_3)]$ with NO has been proven to dissociate NO reversibly in aprotic solvents.[40] On the other hand, the dehydration from either the bound- or terminal-oxygen of the nitrito ligand caused by the electrochemical reduction of $[Cu(ONO)(tpa)]^+$ in H_2O would result in the Cu–O bond cleavage or the formation of an unstable oxygen-bound nitrosyl adduct. Electrochemical reduction of $[Cu(ONO)(tpa)]^+$ may, therefore, be followed by NO dissociation prior to the formation of $[Cu(NO)(tpa)]^+$.

The precursor to N_2O in the reduction of NO_2^- or NO by $[Cu(H_2O)(tpa)]^{2+}$ is not clear under the present electrolysis conditions. Although *cis*-$[Cu(NO)_2(HB(R_2pz)_3)]$ and dimeric $[Cu(\mu_2\text{-}NO)(HB(R_2pz)_3)]_2$ (R= Me, Ph) are proposed as the precursor to N_2O in the reaction of $[Cu(CH_3CN)(HB(R_2pz)_3)]^+$ with NO,[41] hexa-coordinate Cu(I) species such as $[Cu(NO)_2(tpa)]^+$ and $[Cu(NO)(tpa)]_2^{2+}$ are excluded in the present discussion. In place of μ_2-NO_2Cu_2 unit, an N_2O_2 bridged dimmer complex $[(tpa)Cu(N_2O_2)Cu(tpa)]^{2+}$ is also presented as the precursor to the N_2O and $[(tpa)CuOCu(tpa)]^{2+}$ in the reaction of $[Cu(CH_3CN)(tpa)]^+$ and NO[42] in C_2H_5CN at −80 °C. On the other hand, $[Cu(H_2O)(tpa)]^{n+}$ (n=1, 2) has no ability to accelerate decomposition of *trans*-$HN_2O_2^-$ to N_2O in H_2O. Based on the fact that *cis*-$N_2O_2^{2-}$ is much more labile than *trans*-one,[43] the above conflict may be explained by an assumption of formation of either $[(tpa)Cu(N_2O_2)Cu(tpa)]^{2+}$ or $[Cu(N_2O_2)(tpa)]^+$ with a *cis*-N_2O_2 moiety by dimerization of $[Cu(NO)(tpa)]^+$ or successive reactions of $[Cu(NO)(tpa)]^+$ with NO followed by another $[Cu(sol)(tpa)]^+$ (reactions i and ii in Scheme 1). As an alternative pathway, NO_2^- may directly operate in the key process for the N–N bond formation by an addition to $[Cu(NO)(tpa)]^+$ as a proposed mechanism in copper-containing nitrite reductases (reaction iii in Scheme 1).

We thank Dr. Waizumi of I. M. S. for the low-temperature measurements of the X-ray analysis. We are also grateful for the kind help in the final refinement of the X-ray analysis provided by Assistant Professor H. Masuda of Nagoya Institute of Technology. This research was supported by a Grant-in-Aid for Scientific Research on Priority Areas No. 03241106 from the Ministry of Education, Science and Culture.

References

1) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 4th ed, Wiley-Interscience, New York (1986), p. 221.

2) a) J. B. Godwin and T. J. Meyer, *Inorg. Chem.*, **10**, 2150 (1971); b) H. Nagao, H. Nishimura, H. Funato, Y. Ichikawa, F. S. Howell, M. Mukaida, and H. Kakihana, *Inorg. Chem.*, **28**, 3955 (1989).

3) a) P. M. H. Kroneck, J. Beuerle, and W. Schumacher, "Degradation of Environmental Pollutants by Microorganisms and Their Metalloenzymes," ed by H. Sigel and A. Sigel, "Metal Ions in Biological Systems," Marcel Dekker, New York (1992), Vol. 28 p. 455; b) W. G. Zumft, A. Viebrock, and H. Korner, "The Nitrogen and Sulpur Cycles," ed by J. A. Cole and S. J. Ferguson, Cambridge University Press, Cambridge, MA (1988), p. 245; c) S. Suzuki, T. Kohzuma, S. Shidara, K. Ohki, and T. Aida, *Inorg. Chim. Acta*, **208**, 107 (1993); d) T. Kohzuma, S. Takase, S. Shidara, and S. Suzuki, *Chem. Lett.*, **1993**, 149; e) J. W. Godden, S. Turley, D. C. Teller, E. T. Adman, M. Y. Liu, W. J. Payne, and J. LeGall, *Science*, **253**, 438 (1991); f) S. Suzuki, T. Yoshimura, T. Kohzuma, S. Shidara, M. Masuko, T. Sakurai, and H. Iwasaki, *Biochem. Biophys. Res. Commun.*, **164**, 1366 (1989); g) H. Iwasaki and T. Matsubara, *J. Biochem. (Tokyo)*, **69**, 847 (1971); h) R. Timkovich, M. S. Cork, and P. V. Taylor, *J. Biol. Chem.*, **259**, 1577 (1984); i) R. Timkovich, R. Dhesi, K. J. Martinkus, M. K. Robinson, and T. M. Res, *Arch. Biochem. Biophys.*, **215**, 47 (1982).

4) a) J. N. Younathan, K. S. Wood, and T. J. Meyer, *Inorg. Chem.*, **31**, 3280 (1992); b) W. B. Tolman, *Inorg. Chem.*, **30**, 4877 (1991); c) M. R. Rhodes, M. H. Barley, and T. J. Meyer, *Inorg. Chem.*, **30**, 629 (1991); d) G. Denariaz, W. J. Payne, and J. LeGall, *Biochim. Biophys. Acta*, **1056**, 225 (1991); e) M. A. Jackson, J. M. Tiedje, and B. A. Averill, *FEBS Lett.*, **291**, 41 (1991); f) C. L. Hulse, B. A. Averill, and J. M. Tiedje, *J. Am. Chem. Soc.*, **111**, 2322 (1989); g) M. H. Barley, K. J. Takeuchi, and T. J. Meyer, *J. Am. Chem. Soc.*, **108**, 5876 (1986); h) D. F. C. Wharton and S.

T. Weintraub, *Biochem. Biophys. Res. Commun.*, **97**, 236 (1980).

5) a) E. A. E. Garber and T. C. Hollocher, *J. Biol. Chem.*, **257**, 8091 (1982); b) E. Weeg-Aerssens, J. M. Tiedje, and B. A. Averill, *J. Am. Chem. Soc.*, **110**, 6851 (1988); c) E. Aerssens, J. M. Tiedje, and B. A. Averill, *J. Biol. Chem.*, **261**, 9652 (1986); d) B. A. Averill and J. M. Tiedje, *FEBS Lett.*, **138**, 8 (1982).

6) a) C. -H. Kim and T. C. Hollocher, *J. Biol. Chem.*, **259**, 2092 (1984); b) E. A. E. Garber and T. C. Hollocher, *J. Biol. Chem.*, **257**, 4705 (1982); c) C. -H. Kim and T. C. Hollocher, *J. Biol. Chem.*, **258**, 4861 (1983); d) E. A. E. Garber, S. Wehrli, and T. C. Hollocher, *J. Biol. Chem.*, **258**, 3587 (1983).

7) S. Kuwabata, S. Uezumi, K. Tanaka, and T. Tanaka, *Inorg. Chem.*, **25**, 3018 (1986).

8) K. Tanaka, R. Wakita, and T. Tanaka, *J. Am. Chem. Soc.*, **111**, 2428 (1989).

9) K. Tanaka, N. Komeda, and T. Matsui, *Inorg. Chem.*, **30**, 3282 (1991).

10) H. Nasri, Y. Wang, B. H. Huynh, and W. R. Scheidt, *J. Am. Chem. Soc.*, **113**, 717 (1991).

11) 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).

12) a) J. W. Godden, S. Turley, D. C. Teller, E. T. Adman, M. Y. Liu, W. J. Payne, and J. LeGall, *Science*, **153**, 438 (1991); b) E. T. Adman and S. Turley, "In Bioinorganic Chemistry of Copper," ed by K. D. Karlin and Z. Tyeklar, Chapman & Hell Inc., New York (1993), p. 397.

13) N. Komeda, H. Nagao, G. Adachi, M. Suzuki, A. Uehara, and K. Tanaka, *Chem. Lett.*, **1993**, 1521.

14) G. Anderegg and F. Wenk, *Helv. Chim. Acta*, **50**, 2330 (1967).

15) R. R. Jacobson, Z. Tyeklar, K. D. Karlin, and J. Zubieta, *Inorg. Chem.*, **30**, 2035 (1991).

16) Z. Tyeklar, R. R. Jacobson, N. W. Narasappa, N. Murthy, J. Zubieta, and K. D. Karlin, *J. Am. Chem. Soc.*, **115**, 2677 (1993).

17) A. W. Scott, *J. Am. Chem. Soc.*, **49**, 986 (1927).

18) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, U. K. (1974), Vol. IV.

19) DIFABS: N. Walker and D. Stuart, *Acta Crystallogr, Sect. A*, **A39**, 158 (1983).

20) The ν(N–O) band is obscured by a strong absorption band of CD_3CN.

21) R. Allmann, S. Kremer, and D. Jucharzcky, *Inorg. Chim. Acta*, **85**, L19 (1985).

22) F. S. Stephens, *J. Chem. Soc. A*, **1969**, 2081.

23) A. Walsh, B. Walsh, B. Murphy, and B. Hathaway, *J. Acta Crystallogr., Sect. B*, **B37**, 1512 (1981).

24) a) S. Takagi, M. D. Joesten, and P. G. Lenhert, *J. Am. Chem. Soc.*, **10**, 1264 (1975); b) S. Klein and D. Reinen, *J. Solid State Chem.*, **32**, 311 (1980).

25) K. A. Klanderman, W. C. Hamilton, and I. Bernal, *Inorg. Chim. Acta*, **23**, 117 (1977).

26) The cathodic and anodic waves of $[Cu(H_2O)(tpa)]^{2+/+}$ couple are $E_{pc} = -0.03$ and $E_{pa} = +0.05$ V in CH_3CN at −25 °C.

27) a) F. R. Keene, D. J. Salmon, J. L. Walsh, H. D. Abruna, and T. J. Meyer, *Inorg. Chem.*, **19**, 1896 (1980); b) H. Nagao, H. Nishimura, Y. Kitanaka, F. S. Howell, M. Mukaida, and H. Kakihana, *Inorg. Chem.*, **29**, 1694 (1990).

28) G. Anderegg, E. Hubmann, N. G. Podder, and F. Wenk, *Helv. Chim. Acta*, **60**, 123 (1977).

29) S. C. Lee and R. H. Holm, *J. Am. Chem. Soc.*, **115**, 11789 (1993).

30) In the absence of $[Cu(H_2O)(tpa)]^{2+}$, NO_2^- is not reduced up to −1.2 V at pH 7.0.

31) a) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 4th ed, Willey, New York (1980), p. 430; b) G. Stedman, *Adv. Inorg. Chem. Radiochem.*, **22**, 113 (1979).

32) M. Gratzel, S. Taniguchi, and A. Henglein, *Ber. Bunsen-Ges. Phys. Chem.*, **74**, 1003 (1970).

33) NO_2^- is not reduced at all under the electrolysis at −0.4 V in H_2O (pH 7.0).

34) Only gaseous N_2O was analyzed.

35) N_3^- is not reduced by $[Cu(H_2O)(tpa)](ClO_4)_2$ under the electrolysis at −0.40 V in H_2O (pH 7.0).

36) J. A. Halfen and W. B. Tolman, *J. Am. Chem. Soc.*, **116**, 5475 (1994).

37) The CV of $[Cu(H_2O)(tpa)](ClO_4)_2$ showed the $[Cu(H_2O)(tpa)]^{2+/+}$ couple at $E_{pc} = -0.47$ and $E_{pa} = -0.38$ V with 100 $mV\,s^{-1}$ in aqueous phosphate buffer solution at pH 7.0.

38) a) E. L. Loechler, A. M. Schneider, D. B. Schwartz, and T. C. Hollocher, *J. Am. Chem. Soc.*, **109**, 3076 (1987); b) M. N. Hughes and G. Stedman, *J. Chem. Soc.*, **1963**, 1239.

39) W. J. Pleth, "Encyclopedia of Electrochemistry of the Elements VIII," ed by A. J. Bard, M. Dekker, New York (1978), p. 346.

40) a) S. M. Carrier, C. E. Ruggiero, W. B. Tolman, and G. B. Jameson, *J. Am. Chem. Soc.*, **114**, 4407 (1992); b) C. E. Rugiero, S. M. Carrier, W. E. Antholine, J. W. Whittaker, C. J. Cramer, and W. B. Tolman, *J. Am. Chem. Soc.*, **115**, 11285 (1993).

41) C. E. Ruggiero, S. M. Carrier, and W. B. Tolman, *Angew. Chem., Int. Ed. Engl.*, **33**, 895 (1994).

42) P. P. Paul and K. D. Karlin, *J. Am. Chem. Soc.*, **113**, 6331 (1991).

43) E. L. Loechler, A. M. Schneider, D. B. Schwartz, and T. C. Hollocher, *J. Am. Chem. Soc.*, **109**, 3076 (1987).