Inorg. Chem. **1996,** *35,* 6809−6815 **6809**

Structural and Electrochemical Comparison of Copper(II) Complexes with Tripodal Ligands

Hirotaka Nagao,[†] Nobutoshi Komeda,[§] Masao Mukaida,[†] Masatatsu Suzuki,[‡] and Koji Tanaka*,[§]

Department of Chemistry, Faculty of Science and Technology, Sophia University, Kioi-cho, Chiyoda-ku, Tokyo 102, Japan, Department of Chemistry, Faculty of Science, Kanazawa University, Kakumamachi, Kanazawa 920-11, Japan, and Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

Received March 20, 1996[⊗]

A series of copper(II) complexes with tripodal polypyridylmethylamine ligands, such as tris(2-pyridylmethyl)-amine (tpa), ((6-methyl-2-pyridyl)methyl)bis(2-pyridylmethyl)amine (Me$_1$tpa), bis((6-methyl-2-pyridyl)methyl)-(2-pyridylmethyl)amine (Me$_2$tpa), and tris((6-methyl-2-pyridyl)methyl)amine (Me$_3$tpa), have been synthesized and characterized by X-ray crystallography. [Cu(H$_2$O)(tpa)](ClO$_4$)$_2$ (**1**) crystallized in the monoclinic system, space group $P2_1/a$, with $a = 15.029(7)$ Å, $b = 9.268(2)$ Å, $c = 17.948(5)$ Å, $\beta = 113.80(3)°$, and $Z = 4$ ($R = 0.061$, $R_w = 0.059$). [CuCl(Me$_1$tpa)]ClO$_4$ (**2**) crystallized in the triclinic system, space group $P\bar{1}$, with $a = 13.617(4)$ Å, $b = 14.532(4)$ Å, $c = 12.357(4)$ Å, $\alpha = 106.01(3)°$, $\beta = 111.96(2)°$, $\gamma = 71.61(2)°$, and $Z = 4$ ($R = 0.054$, $R_w = 0.037$). [CuCl(Me$_2$tpa)]ClO$_4$ (**3**) crystallized in the monoclinic system, space group $P2_1/n$, with $a = 19.650(4)$ Å, $b = 13.528(4)$ Å, $c = 8.55(1)$ Å, $\beta = 101.51(5)°$, and $Z = 4$ ($R = 0.071$, $R_w = 0.050$). [CuCl(Me$_3$tpa)]-[CuCl$_2$(Me$_3$tpa)]ClO$_4$ (**4**) crystallized in the monoclinic system, space group $P2_1/a$, with $a = 15.698(6)$ Å, $b = 14.687(7)$ Å, $c = 19.475(4)$ Å, $\beta = 97.13(2)°$, and $Z = 4$ ($R = 0.054$, $R_w = 0.038$). All the Cu atoms of **1**−**4** have pentacoordinate geometries with three pyridyl and one tertiary amino nitrogen atoms, and a chloride or aqua oxygen atom. Nitrite ion coordinated to the Cu(II) center of Me$_1$tpa, Me$_2$tpa, and Me$_3$tpa complexes with only oxygen atom to form nitrito adducts. The cyclic voltammograms of [Cu(H$_2$O)(Me$_n$tpa)]$^{2+}$ ($n = 0$, 1, 2, and 3) in the presence of NO$_2^-$ in H$_2$O (pH 7.0) revealed that the catalytic activity for the reduction of NO$_2^-$ increases in the order Me$_3$tpa $\ll$ Me$_2$tpa $\ll$ Me$_1$tpa $<$ tpa complexes.

Introduction

Coordination chemistry of copper complexes is a subject of continuing importance in connection with the structures and the reactivities of the active site in copper-containing metalloproteins. Along this line, a variety of mono- and dinuclear copper complexes with tripodal ligands such as NL$_3$ type (L = pyridine,[1−15] phenolate,[5,7] benzimidazole,[5,13,16,17] quinoline,[6,8] imidazole,[9−14] pyrazole,[12,13,18,19] benzothiazole,[22] thioester,[23] histidine,[24] and azomethine[25,26]) and PL′$_3$ type (L′ = imidazolyl[27]) have been synthesized. The redox behavior of Cu(II)/

---

* Author to whom correspondence should be addressed.

[†] Sophia University.

[‡] Kanazawa University.

[§] Institute for Molecular Science.

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1996.

(1) (a) Sanyal, I.; Ghosh, P.; Karlin, K. D. *Inorg. Chem.* **1995**, *34*, 3050. (b) Harata, M.; Jitsukawa, K.; Masuda, H.; Einaga, H. *Chem. Lett.* **1995**, 61. (c) Karlin, K. D.; Nanthakumar, A.; Fox, S.; Murthy, N. N.; Ravi, N.; Huynh, B. H.; Orosz, R. D.; Day, E. P. *J. Am. Chem. Soc.* **1994**, *116*, 4753. (d) Nanthakumar, A.; Fox, S.; Murthy, N. N.; Karlin, K. D. *J. Am. Chem. Soc.* **1993**, *115*, 8513. (e) Jiang, F.; Conry, R. R.; Bubacco, L.; Tyeklar, Z.; Jacobson, R. R.; Karlin, K. D.; Peisach, J. *J. Am. Chem. Soc.* **1993**, *115*, 2093. (f) Fox, S.; Nanthakumar, A.; Wei, N.; Murthy, N. N.; Karlin, K. D. *Pure Appl. Chem.* **1993**, *65*, 2335. (g) Uozumi, K.; Hatashi, Y.; Suzuki, M.; Uehara, A. *Chem. Lett.* **1993**, 963. (h) Nanthakumar, A.; Nasir, M. S.; Karlin, K. D. *J. Am. Chem. Soc.* **1992**, *114*, 6564. (i) Jacobson, R. R.; Tyeklar, Z.; Karlin, K. D. *Inorg. Chim. Acta* **1991**, *181*, 111. (j) Baek, H. K.; Karlin, K. D.; Holwerda, R. A. *Inorg. Chem.* **1986**, *25*, 2347. (k) Kokoszka, G.; Karlin, K. D.; Padula, F.; Baranowski, J.; Goldstein, C. *Inorg. Chem.* **1984**, *23*, 4378. (l) Baek, H. K.; Holwerda, R. A. *Inorg. Chem.* **1983**, *22*, 3452.

(2) Chuang, C.; Lim, K.; Chen, Q.; Zubieta, J.; Canary, J. W. *Inorg. Chem.* **1995**, *34*, 2562.

(3) Komeda, N.; Nagao, H.; Kushi, Y.; Adachi, G.; Suzuki, M.; Uehara, A.; Tanaka, K. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 581.

(4) Malachowski, M. R.; Huynh, H. B.; Tomlinson, L. J.; Kelly, R. S.; Furbee jun, J. W. *J. Chem. Soc., Dalton Trans.* **1995**, 31.

(5) Uma, R.; Viswanathan, R.; Palaniandavar, M.; Laksminarayanan, M. *J. Chem. Soc., Dalton Trans.* **1994**, 1219.

(6) Wei, N.; Murthy, N. N.; Karlin, K. D. *Inorg. Chem.* **1994**, *33*, 6093.

(7) Adams, H.; Bailey, N. A.; Rodriguez de Barbarin, C. O.; Fenton D. E.; He, Q.-Y. *J. Chem. Soc., Dalton Trans.* **1995**, 2323.

(8) Wei, N.; Murthy, N. N.; Chen, Q.; Zubieta, J.; Karlin, K. D. *Inorg. Chem.* **1994**, *33*, 1953.

(9) Tyeklar, Z.; Jacobson, R. R.; Wei, N.; Murthy, N. N.; Zubieta, J.; Karlin. K. D. *J. Am. Chem. Soc.* **1993**, *115*, 2677.

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

(11) (a) Paul, P. P.; Karlin, K. D. *J. Am. Chem. Soc.* **1991**, *113*, 6331. (b) Paul, P. P.; Tyeklar, Z.; Farooq, A.; Karlin, K. D.; Liu, S.; Zubieta, J. *J. Am. Chem. Soc.* **1990**, *112*, 2430.

(12) Oberhausen, K. J.; O'Brien, R. J.; Richardson, J. F.; Buchanan, R. M. *Inorg. Chim. Acta* **1990**, *173*, 145.

(13) Oka, H.; Nakao, Y.; Suzuki, S.; Mori, W.; Kinoshita, I.; Ooi, S.; Ichimura, A. *Inorg. Chim. Acta* **1989**, *165*, 111.

(14) Karlin, K. D.; Hayes, J. C.; Juen, S.; Hutchison, J. P.; Zubieta, J. *Inorg. Chem.* **1982**, *21*, 4106.

(15) Karlin, K. D.; Hayes, J. C.; Hutchinson, J. P.; Hyde, J. R.; Zubueta, J. *Inorg. Chim. Acta* **1982**, *64*, L219.

(16) (a) Satcher, Jr., J. H.; Droege, M. W.; Weakley, T. J. R.; Taylor, R. T. *Inorg. Chem.* **1995**, *34*, 3317. (b) Pandey, H. N.; Sharma, Y. S.; Mathur, P. *Polyhedron* **1992**, *11*, 2631. (c) Lu, Z.-R.; Yin, Y.-Q.; Jin, D.-S. *J. Mol. Catal.* **1991**, *70*, 391.

(17) Nakao, Y.; Onoda, M.; Sakurai, T.; Nakahara, A.; Kinoshita, I.; Ooi, S. *Inorg. Chim. Acta* **1988**, *151*, 55.

(18) Anthony, G. J.; Koolhaas, A.; Driessen, W. L.; Reedijk, J.; Kooijman, H.; Spek, A. L. *J. Chem. Soc., Chem. Commun.* **1995**, 517.

(19) Chen, S.; Richardson, J. F.; Buchanan, R. M. *Inorg. Chem.* **1994**, *33*, 2376.

(20) (a) Malachowski, M. R.; Tomlinson, L. J.; Davidson, M. G.; Hall, M. J. *J. Coord. Chem.* **1992**, *25*, 171. (b) Driessen, W. L.; Wiesmeijer, W. G. R.; Schipper-Zablotskaja, M.; De Graaff, R. A. G.; Reedijk, J. *Inorg. Chim. Acta* **1989**, *162*, 233. (c) Malachowski, M. R.; Davidson, M. G.; Hoffman, J. N. *Inorg. Chim. Acta* **1989**, *157*, 91.

(21) Sorrell, T. N.; Jameson, D. L. *Inorg. Chem.* **1982**, *21*, 1014.

(22) Pandey, H. N.; Mathur, P. *Indian J. Chem.* **1995**, *34*, 186.

S0020-1669(96)00303-5 CCC: $12.00 © 1996 American Chemical Society

Cu(I) couples of those complexes[2,5,6,8,12,13,17,19,21,22,28] and the interaction with O_2, NO, and NO_2^- have been studied from the standpoint of structural models of Cu−proteins. On the other hand, catalytic activity toward reduction of NO_2^- as functional models of copper-containing NO_2^- reductases have hardly been discussed so far.

This work undertakes to elucidate the relationship between the structural changes and the redox potential of $[CuX(Me_n tpa)]^{m+}$; X = Cl, H_2O; $m = 1, 2$; $n = 0, 1, 2, 3$) caused by successive introduction of three methyl groups into the 6-position of pyridine moieties of the tpa ligand and the catalytic ability of these four Cu(II) complexes toward the reduction of NO_2^- in H_2O (pH 7.0). A part of this work has been reported elsewhere.[3]

Experimental Section

Materials. $[Cu(H_2O)(tpa)](ClO_4)_2$,[10] $[CuCl(tpa)]ClO_4$,[14] $[Cu(NO_2)(tpa)]PF_6$, and $[Cu(ONO)(tpa)]PF_6$ [3] were prepared by the modification of methods in the literature. Acetonitrile was purified by distillation over CaH_2. All other chemicals were commercially available and used without further purification.

Physical Measurements. IR spectra were obtained as KBr pellets and CD_3CN solutions using a Shimadzu FTIR-8100 spectrophotometer. Elemental analyses were performed at the Chemical Materials Center of the Institute for Molecular Science and the Sophia University Analytical Facility. ^1H and ^{13}C NMR spectra were measured on a JEOL GX400 spectrophotometer. Mass and FAB-mass spectra were obtained on a JEOL JMS-SX102A and a Shimadzu/Kratos Concept 1S. Electrochemical measurements were performed in a cell equipped with a glassy-carbon working electrode ($\phi = 3$ mm), a Pt-wire auxiliary electrode, an Ag|AgCl reference electrode, and a nozzle for bubbling of N_2. 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.

Synthesis of Ligands. Although the preparations of Me_1tpa, Me_2tpa, and Me_3tpa were reported by Mota et al.,[29] we prepared them by different methods, described below.

((6-Methyl-2-pyridyl)methyl)amine (L-1). Hydroxylamine hydrochloride (7.6 g, 0.11 mol) was dissolved in a minimum amount of water, to which was added 6-methyl-2-pyridinecarboxaldehyde (12.1 g, 0.1 mol) in 40 mL of methanol. Oxime formed was deposited as a white powder. To this suspension was added 1 g of 5% Pd−C and the oxime was hydrogenated at 45 °C under an atmospheric pressure of H_2 with vigorous stirring. After hydrogenated, 5% Pd−C was removed by filtration and the filtrate was evaporated almost to dryness under reduced pressure and the residue was dissolved into water. The aqueous solution was made strongly alkaline by addition of NaOH, giving a brown oil, which was extracted with chloroform. The extract was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was fractionally distilled to afford **L-1** as a colorless oil: bp 62 °C (20 mmHg). Yield: 8.8 g (72%). ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 2.54 (3H, s, CH_3), 3.93 (2H, s, CH_2), 7.01 (1H, d, pyH), 7.08 (1H, d, pyH), 7.52 (1H, t, pyH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 24.4 (CH_3), 47.9 (CH_2), 118.0 (py), 121.2 (py), 136.7 (py), 157.9 (py), 161.3 (py). MS: *m/z* 122 $[M]^+$.

Bis((6-methyl-2-pyridyl)methyl)amine (L-2). 6-Methyl-2-pyridinecarboxaldehyde (12.1 g, 0.1 mol) was added to **L-1** in 100 mL of methanol, to which sodium borohydride (5.0 g, 0.08 mol) was added with stirring. The resulting solution was stirred at room temperature for 12 h and then acidified by addition of concentrated hydrochloric acid to quench excess hydride. The solution was evaporated almost to dryness under reduced pressure. The residue was dissolved into water, and the resulting solution was made alkaline by addition of Na_2CO_3. The dark brown oil that separated was extracted with chloroform. The extract was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was distilled and the distillate was purified as described in the literature.[29] Yield: 12.5 g (55%). ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.54 (6H, s, CH_3), 3.94 (4H, s, CH_2), 7.01 (2H, d, pyH), 7.17 (2H, d, pyH), 7.52 (2H, t, pyH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 24.5 (CH_3), 55.0 (CH_2), 119.1 (py), 121.4 (py), 136.6 (py), 157.9 (py), 159.1 (py). MS: *m/z* 227 $[M]^+$.

Bis((6-methyl-2-pyridyl)methyl)(2-pyridylmethyl)amine (Me_2tpa). Sodium cyanoborohydride (1.63 g, 0.026 mol) was added dropwise to a cold mixture of 2-pyridinecarboxaldehyde (3.53 g, 0.033 mol), **L-2** (6.82 g, 0.030 mol), and acetic acid (4.2 g, 0.07 mol) in 100 mL of methanol with stirring. The resulting solution was stirred at room temperature for 3 days, then acidified by addition of concentrated hydrochloric acid to quench excess hydride, and evaporated almost to dryness under reduced pressure. The residue was dissolved into water and the resulting solution was made alkaline by addition of Na_2CO_3. A dark brown oil separated and was extracted with chloroform. The extract was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure to afford a brownish solid product. It was recrystallized from ligroin (bp 80−100 °C). Yield: 7.1 g (74%). ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.56 (6H, s, CH_3), 3.90 (4H, s, CH_2), 3.93 (2H, s, CH_2), 7.03 (2H, d, pyH), 7.18 (1H, t, pyH), 7.47 (2H, d, pyH), 7.59 (2H, t, pyH), 7.66 (1H, d, pyH), 7.69 (1H, t, pyH), 8.56 (1H, d, pyH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 24.4 (CH_3), 60.2 (CH_2), 60.3 (CH_2), 119.5 (py), 121.4 (py), 121.9 (py), 122.8 (py), 136.3 (py), 136.6 (py), 149.1 (py), 157.6 (py), 159.0 (py), 159.7 (py). MS: *m/z* 318 $[M]^+$.

((6-Methyl-2-pyridyl)methyl)bis(2-pyridylmethyl)amine (Me_1tpa). This was prepared by a method similar to that for Me_2tpa using 6-methyl-2-pyridinecarboxaldehyde (13.3 g, 0.11 mol) and bis(2-pyridylmethyl)amine (19.9 g, 0.10 mol) instead of 2-pyridinecarboxaldehyde and bis(6-methyl-2-pyridylmethyl)amine, respectively. Sodium cyanoborohydride (5.02 g, 0.08 mol) was used. The crude product was recrystallized from ligroin (bp 80−100 °C) to give pale yellow crystals. Yield: 13.5 g (44%). ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.52 (3H, s, CH_3), 3.86 (2H, s, CH_2), 3.88 (4H, s, CH_2), 6.99 (1H, d, pyH), 7.14 (2H, t, pyH), 7.42 (1H, d, pyH), 7.55 (1H, t, pyH), 7.59 (2H, d, pyH), 7.65 (2H, t, pyH), 8.52 (2H, d, pyH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 24.4 (CH_3), 60.2 (CH_2), 60.3 (CH_2), 119.6 (py), 121.4 (py), 121.9 (py), 122.9 (py), 136.3 (py), 136.6 (py), 149.1 (py), 157.7 (py), 158.8 (py), 159.6 (py). MS: *m/z* 304 $[M]^+$.

Tris((6-methyl-2-pyridyl)methyl)amine (Me_3tpa). This was prepared by a method similar to that for Me_2tpa using bis(6-methyl-2-pyridylmethyl)amine (6.82 g, 0.030) and 6-methyl-2-pyridinecarboxaldehyde (4.0 g, 0.033 mol) instead of 2-pyridinecarboxaldehyde. Sodium cyanoborohydride (1.51 g, 0.024 mol) was used. The crude product was recrystallized from ligroin (bp 80−100 °C) to give pale yellow crystals. Yield: 6.8 g (68%). ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.56 (9H, s, CH_3), 3.85 (6H, s, CH_2), 6.98 (3H, d, pyH), 7.42 (3H, d, pyH), 7.53 (3H, t, pyH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 24.4 (CH_3), 60.3 (CH_2), 119.5 (py), 121.3 (py), 136.6 (py), 157.6 (py), 159.1 (py). MS: *m/z* 332 $[M]^+$.

Synthesis of Complexes. *Caution! Although the complexes as perchlorate salts described below are stable, they are potentially explosive and should be handled with care.*

$[Cu(H_2O)(L)](ClO_4)_2$ (L = Me_1tpa, Me_2tpa, and Me_3tpa). A series of aqua Cu(II) complexes were synthesized by a modified method of $[Cu(H_2O)(tpa)](ClO_4)_2$.[10] An addition of L (1.0 mmol) to a stirred C_2H_5OH (20 cm^3) solution containing $Cu(ClO_4)_2 \cdot 5H_2O$ (1.0 mmol) afforded a greenish blue precipitate of $[Cu(H_2O)(L)](ClO_4)_2$. $[Cu(H_2O)(Me_2tpa)](ClO_4)_2$ and $[Cu(H_2O)(Me_3tpa)](ClO_4)_2$ were recrystallized from CH_2Cl_2/ether. Yield: *ca.* 70%. Anal. Calcd for $[Cu(H_2O)(Me_1tpa)](ClO_4)_2 \cdot 1.5H_2O$: C, 37.30; H, 4.12; N, 9.16. Found: C, 37.40; H, 4.07; N, 9.01. Calcd for $[Cu(H_2O)(Me_2tpa)](ClO_4)_2 \cdot 0.5CH_2Cl_2$: C, 38.39; H, 3.93; N, 8.74. Found: C, 38.49; H, 3.69; N, 8.87.

---

(23) (a) Nishida, Y.; Takahashi, K. *Inorg. Chem.* **1988**, *27*, 1406. (b) Suzuki, M.; Kanatomi, H.; Koyama, H.; Murase, I. *Inorg. Chim. Acta* **1980**, *44*, L41.

(24) Goldfarb, D.; Fauth, J.-M.; Tor, Y.; Shanzer, A. *J. Am. Chem. Soc.* **1991**, *113*, 1941.

(25) McLachlan, G. A.; Fallon, G. D.; Martin, R. L.; Spiccia, L. *Inorg. Chem.* **1995**, *34*, 254.

(26) Fenton, D. E.; Westwood, G. P.; Bashall, A.; McPartlin, M.; Scowen, I. J. *J. Chem. Soc., Dalton Trans.* **1994**, 2213.

(27) Sorrell, T. N.; Allen, W. E.; White, P. S. *Inorg. Chem.* **1995**, *34*, 952.

(28) Addison, A. W. *Inorg. Chim. Acta* **1989**, *162*, 217.

(29) Da Mota, M. M.; Rogers, J.; Nelson, S. M. *J. Chem. Soc. A* **1969**, 2036.

Table 1. Crystallographic Data

	1	**2**	**3**	**4**
formula	$C_{18}H_{20}N_4O_9Cl_2Cu$	$C_{19}H_{20}N_4O_4Cl_2Cu$	$C_{20}H_{22}N_4O_4Cl_2Cu$	$C_{42}H_{48}N_8O_4Cl_4Cu_2$
fw	570.83	502.84	516.87	997.80
space group (No.)	$P2_1/n$ (14)	$P\bar{1}$ (2)	$P2_1/n$ (14)	$P2_1/a$ (14)
a/Å	15.029(7)	13.617(4)	19.650(4)	15.698(6)
b/Å	9.268(2)	14.532(4)	13.528(4)	14.687(7)
c/Å	17.948(5)	12.357(4)	8.55(1)	19.475(4)
α/deg	90	106.01(3)	90	90
β/deg	113.80(3)	111.96(2)	101.51(5)	97.13(2)
γ/deg	90	71.61(2)	90	90
V/Å^3	2287(1)	2117(1)	2227(2)	4455(2)
ρ_{calc}/g cm^{-3}	1.66	1.58	1.54	1.49
Z	4	4	4	4
μ/cm^{-1}	12.46	13.18	12.54	12.45
radiation	graphite-monochromated Mo Kα ($\lambda = 0.710\ 69$ Å)			
T, °C	23	23	23	23
R/R_w[a]	0.061/0.059	0.054/0.037	0.071/0.050	0.054/0.038

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, $w = 1/\sigma^2(F_o)$.

Calcd for $[Cu(H_2O)(Me_3tpa)](ClO_4)_2$: C, 41.15; H, 4.28; N, 9.14. Found: C, 41.13; H, 4.25; N, 9.13.

$[CuCl(L)]ClO_4$ (L = Me_1tpa, Me_2tpa, and Me_3tpa). Addition of KCl (2.0 mmol) to a stirred H_2O/C_2H_5OH (2:5 v/v, 35 cm^3) solution containing $Cu(ClO_4)_2\cdot 5H_2O$ (1.0 mmol) and L (1.0 mmol) afforded a blue precipitate of $[CuCl(L)]ClO_4$. Yield: *ca*. 80%. Anal. Calcd for $[CuCl(Me_1tpa)]ClO_4$: C, 45.38; H, 4.01; N, 11.14. Found: C, 45.30; H, 4.12; N, 11.10. Calcd for $[CuCl(Me_2tpa)]ClO_4$: C, 46.48; H, 4.29; N, 10.84. Found: C, 46.13; H, 4.22; N, 10.71. Calcd for $[CuCl(Me_3tpa)][CuCl_2(Me_3tpa)]ClO_4$: C, 50.56; H, 4.85; N, 11.23. Found: C, 50.59; H, 4.84; N, 11.17.

$[Cu(ONO)(L)]PF_6$ (L = Me_1tpa, Me_2tpa, and Me_3tpa). Addition of NH_4PF_6 (2.0 mmol) to a stirred H_2O/C_2H_5OH (2:5 v/v, 35 cm^3) solution containing $(CH_3COO)_2Cu\cdot H_2O$ (1.0 mmol), L (1.0 mmol), and $NaNO_2$ (2.0 mmol) afforded a green precipitate of $[Cu(ONO)(L)]PF_6$. Yield: *ca*. 60%. Anal. Calcd for $[Cu(ONO)(Me_1tpa)]PF_6$: C, 40.83; H, 3.61; N, 12.53. Found: C, 40.71; H, 3.52; N, 12.16. Calcd for $[Cu(ONO)(Me_3tpa)]PF_6$: C, 42.97; H, 4.12; N, 11.93. Found: C, 42.99; H, 4.11; N, 11.86. FAB-Mass Spectrum for $[Cu(ONO)(Me_2tpa)]PF_6$: 427[M-PF_6]$^+$. IR spectral data (KBr): $[Cu(ONO)(Me_1tpa)]PF_6$, ν(N=O) 1428 cm^{-1} and ν(N−O) 1076 cm^{-1}; $[Cu(ONO)(Me_2tpa)]PF_6$, ν(N=O) 1410 cm^{-1} and ν(N−O) 1098 cm^{-1}; $[Cu(ONO)(Me_3tpa)]PF_6$, ν(N=O) 1400 cm^{-1} and ν(N−O) 1094 cm^{-1}.

X-ray Crystallographic Data Collection and Refinement of the Structures. A single crystal was mounted on a glass fiber. The diffraction intensities were collected with graphite-monochromated Mo Kα radiation on Enraf-Nonius FR-590, Rigaku AFC5S, or Rigaku AFC5R diffractometer at 23 °C and the $\omega-2\theta$ scan technique to a $2\theta_{max}$ value of 50.0° or 55.0°. Crystallographic data for **1**−**4** are given in Table 1. All of the calculations were carried out on an IRIS Indigo computer of the Silicon Graphics corporation, using the TEXSAN crystallographic software package of the Molecular Structure Corp. The structures were solved by direct methods and expanded using Fourier techniques. Empirical absorption corrections using DIFABS[30] were applied after a full isotropic refinement of non-hydrogen atoms. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were included by no refined. Atomic scattering factors were taken from tables.[31] Complete information on collected data and refinement and atomic coordinates, are included as Supporting Information.

Results and Discussion

Synthesis of Copper(II) Complexes Containing Nitrite Ligand. A series of $[CuCl(Me_ntpa)]^+$ ions (n = 1, 2, 3) were prepared in a manner similar to $[CuCl(tpa)]^+$. The reaction of $[Cu(H_2O)(tpa)]^{2+}$ with NO_2^- produced $[Cu(ONO)(tpa)]^+$ and $[Cu(NO_2)(tpa)]^+$, and these nitrito and nitro isomers exist as an equilibrium mixture in solutions.[3] On the other hand, the reaction of NO_2^- with Cu(II) complexes with Me_1tpa, Me_2tpa, and Me_3tpa ligands selectively produced the nitrito isomers, $[Cu(ONO)(Me_ntpa)]^+$ (n = 1, 2, 3), since only the ν(N=O) and ν(N−O) bands of the nitrito isomers were observed in the IR spectra of the crude and purified products (1428 and 1076 cm^{-1} for the Me_1tap complex, 1410 and 1098 cm^{-1} for the Me_2tap complex, and the 1400 and 1094 cm^{-1} for Me_3tap complex). The IR spectra of these complexes in CD_3CN also displayed only the ν(N=O) band at almost same wavenumber as those in the solid state,[32] and neither $\nu_{asym}(NO_2)$ nor $\nu_{sym}(NO_2)$ band of a nitrito isomer was detected in the regions of 1470−1370 and 1340−1320 cm^{-1}, respectively.[33]

Electrochemical Behavior of Copper(II) Complexes. Controlled-potential electrolysis of $[Cu(H_2O)(tpa)]^{2+}$ in the presence of NO_2^- at −0.40 V in H_2O (pH 7.0) catalytically produces NO and N_2O, in which both $[Cu(ONO)(tpa)]^+$ and $[Cu(NO_2)(tpa)]^+$ play the active species in the reduction.[3] Stoichiometrical NO evolution from $LCuNO_2$ (L = 1,4,7-triisopropyl-1,4,7-triazacyclononane) is also demonstrated by treatment of the complex with 2 equiv of glacial acetic acid in CH_2Cl_2.[34] The redox behavior of $[Cu(H_2O)(Me_ntpa)]^{2+}$ (n = 0, 1, 2, 3) was examined in the absence and the presence of NO_2^- to evaluate the catalytic activity of these complexes for the reduction of NO_2^-. The cyclic voltammograms (CVs) of $[Cu(H_2O)(Me_ntpa)]^{2+}$ in aqueous solution (pH 7) are depicted as solid lines in Figure 1. The electrochemical parameters in H_2O and CH_3CN are summarized in Table 2.[35] As depicted in Figure 1, the cathodic and anodic waves of the Cu(I)/Cu(II) redox couples unexpectedly shift to positive potentials in the order, tpa < Me_1tpa < Me_2tpa < Me_3tpa complexes. The peak separation ($\Delta E = E_{pa} - E_{pc}$) of the redox couples increases in the same order. The $E_{1/2}$ and ΔE values of the $[CuCl(Me_ntpa)]^{+/0}$ and the $[Cu(H_2O)(Me_ntpa)]^{2+/+}$ couples in CH_3CN also showed the same tendency. Thus, the electron density of the copper center and the reversibility of the Cu(II)/Cu(I) redox couple of these complexes decrease with an increase in the number of methyl group in the Me_ntpa ligand. The CVs of $[Cu(H_2O)(Me_ntpa)]^{2+}$

---

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

(31) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

(32) The ν(N−O) bands were obscured by the strong absorption band of CD_3CN.

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

(34) Halfen, J. A.; Mahapatra S.; Wilkinson, E. C.; Gengenbach, A. J.; Young, V. G., Jr.; Que, L., Jr.; Tolman, W. B. *J. Am. Chem. Soc.* **1996**, 118, 763.

(35) The CVs of $[Cu(H_2O)(Me_ntpa)]^{2+}$ and $[CuCl(Me_ntpa)]^+$ were completely consistent with each other in H_2O (pH 7). Thus, $[CuCl(Me_ntpa)]^+$ is converted to $[Cu(H_2O)(Me_ntpa)]^{2+}$ in H_2O.

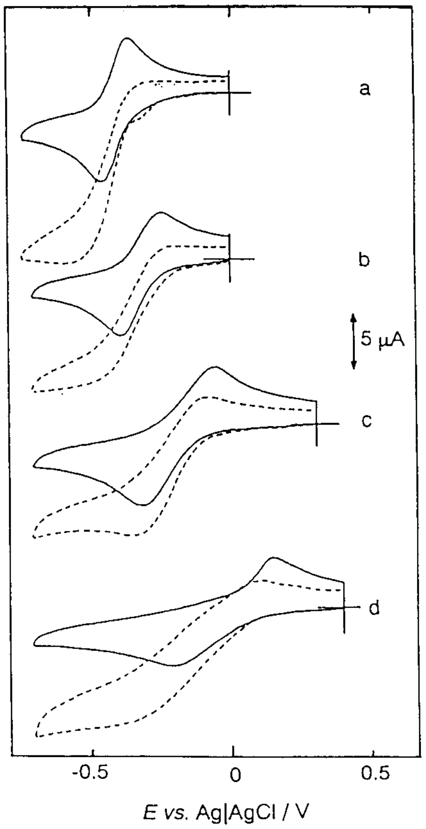

Figure 1. Cyclic voltammograms of $[Cu(H_2O)(tpa)](ClO_4)_2$ (a), $[Cu(H_2O)(Me_1tpa)](ClO_4)_2$ (b), $[Cu(H_2O)(Me_2tpa)](ClO_4)_2$ (c), and $[Cu(H_2O)(Me_3tpa)](ClO_4)_2$ (d) in the absence (solid lines) and the presence of $NaNO_2$ (dotted lines) in H_2O at pH 7.0. $[NO_2^-]/[complex] = 1.5$ for (a), 50 for (b), 500 for (c), and 1500 for (d).

Table 2. Redox Potentials (*vs* Ag|AgCl) of $[Cu(H_2O)L](ClO_4)_2$ in H_2O (pH 7.0) and CH_3CN[a]

L	E_{pa}/V	E_{pc}/V	$E_{1/2}{}^b$/V	ΔE/V
tpa	−0.37	−0.47	−0.42	0.10
	(0.07)	(−0.02)	(0.03)	(0.09)
Me_1tpa	−0.27	−0.38	−0.33	0.11
	(0.13)	(0.04)	(0.09)	(0.09)
Me_2tpa	−0.08	−0.31	−0.20	0.23
	(0.26)	(0.12)	(0.19)	(0.14)
Me_3tpa	0.16	−0.23	−0.04	0.39
	(0.60)	(0.27)	(0.44)	(0.33)

[a] The value in parentheses is in CH_3CN. [b] $E_{1/2} = (E_{pa} + E_{pc})/2$.

in the presence of $NaNO_2$ in H_2O (pH 7) are also depicted by dotted lines in Figure 1. An addition of 1.5 equiv of $NaNO_2$ to the aqueous solution of $[Cu(H_2O)(tpa)]^{2+}$ causes a strong cathodic current due to the reduction of NO_2^- at more negative potentials than the threshold potential of the cathodic waves of the Cu(II)/Cu(I) couples (Figure 1a). Complete disappearance of the anodic wave in the reverse potential sweep also shows the high catalytic activity of the complex toward NO_2^- reduction producing N_2O through NO (eqs 1 and 2). Similarly,

$$NO_2^- + 2H^+ + e^- \rightarrow NO + H_2O \qquad (1)$$

$$2NO_2^- + 6H^+ + 4e^- \rightarrow N_2O + 3H_2O \qquad (2)$$

$[Cu(H_2O)(Me_1tpa)]^{2+}$ in the presence of 50 equiv of $NaNO_2$ displays a catalytic current due to the reduction of NO_2^- (Figure 1b). On the basis of the current density depending on the mole ratios of $[NO_2^-]/[Cu^{2+}]$, the catalytic activity of $[Cu(H_2O)(Me_1tpa)]^{2+}$ toward the reduction of NO_2^- is estimated to be less than $^1/_{40}$ compared with that by $[Cu(H_2O)(tpa)]^{2+}$. The catalytic activity of $[Cu(H_2O)(Me_2tpa)]^{2+}$ and $[Cu(H_2O)(Me_3tpa)]^{2+}$ for the reduction of NO_2^- further decreased, because the increases in cathodic currents at more negative potentials than the cathodic waves of the $[Cu(H_2O)(Me_2tpa)]^{2+/+}$ and $[Cu(H_2O)(Me_3tpa)]^{2+/+}$ couples are quite small even in the presence of 5.0×10^2 and 1.5×10^3 molar excesses of NO_2^- (Figure 1c,d). Thus, the catalytic activity for the reduction of NO_2^- by $[Cu(H_2O)(Me_ntpa)]^{2+}$ ($n = 0, 1, 2, 3$) decreases in the order tpa > $Me_1tpa \gg Me_2tpa \gg Me_3tpa$ complexes. In fact, the controlled-potential electrolysis of $[Cu(H_2O)(Me_1tpa)](ClO_4)_2$ in the presence of a 75 molar excess of NO_2^- at −0.40 V in H_2O (pH 7.0) catalytically produced N_2O and a small amount of NO, similar to that with $[Ru(H_2O)(tpa)]^{2+}$,[3] while $[Cu(H_2O)(Me_2tpa)](ClO_4)_2$ hardly catalyzed the reduction of NO_2^- under the similar electrolysis conditions. It should be noticed that the order of the catalytic activity does not result from the steric hindrance of methyl groups of the Me_ntpa ligand for the attack of NO_2^- to the Cu^{2+} center, since $[Cu(ONO)(Me_ntpa)]^+$ ions ($n = 0, 1, 2, 3$) are smoothly formed in the reaction of $[Cu(H_2O)(Me_ntpa)]^+$ with NO_2^-.[36]

Structures of Copper(II) Complexes. Single crystals of $[Cu(H_2O)(tpa)](ClO_4)_2$ (**1**), $[CuCl(Me_1tpa)]ClO_4$ (**2**), $[CuCl(Me_2tpa)]ClO_4$ (**3**), and $[CuCl(Me_3tpa)][CuCl_2(Me_3tpa)]ClO_4$ (**4**) were obtained by recrystallization of the crude complexes from CH_2Cl_2/Et_2O or slow evaporation of the synthesized solution. Except for the neutral $[CuCl_2(Me_3tpa)]$ unit in **4**, all the Cu(II) atoms of **1**−**4** are pentacoordinated structures with three pyridyl nitrogens, one amino nitrogen, and a chloride or oxygen atom of H_2O. Selected bond distances and angles of all complexes are summarized in Table 3. The molecular structures of copper complexes are shown in Figure 2−6. The structures of the present pentacoordinated Cu(II) complexes are trigonal bipyramid, square pyramid, and the intermediate between them. The changes in the bond distances in the series $[CuCl(Me_ntpa)]^+$ ($n = 0, 1, 2, 3$) are depicted in Figure 7.

Furthermore, a structural index parameter τ $(=(\beta - \alpha)/60)$ introduced by Reedijk,[37] where α and β represent two basal angles ($\beta \geq \alpha$), was also adopted to systematize the change in the geometries of the complexes. A perfect trigonal-bipyramid is associated with $\alpha = 120°$ and $\beta = 180°$ ($\tau = 1$), and idealized square pyramidal geometries are defined as $\alpha = \beta = 180°$ ($\tau = 0$). In the real square pyramidal structures, metal atoms usually are located out of the equatorial plane toward the axial bond. The C_{4v} geometries still can be characterized by $\tau \approx 0$ ($\alpha \approx \beta < 180°$). The structural parameters α, β, and τ are summarized in Table 4.

The geometry of **1** is expressed by an almost idealized trigonal bipyramid with $\tau = 0.97$. Three pyridyl nitrogen atoms equivalently coordinate to Cu^{2+} in the equatorial plane (2.054(6), 2.038(7), and 2.069(6) Å for the Cu−N2, −N3, and −N4 bonds, and 119.9(2), 118.2(3), and 116.8(2)° for three N−Cu−N angles), and amino nitrogen and aqua oxygen atoms are in the axial positions (Figure 2). A series of $[CuX(tpa)]^+$ ions (X = Cl, F, ONO, NO_2) also have the trigonal bipyramidal structure, and the Cu−N bond distances in the basal plane of those complexes are also close to those of **1**. On the other hand, the Cu−N1 (amino nitrogen) bond distance (1.941(6) Å) is significantly shorter than that of $[CuX(tpa)]^+$ (2.050(6), 2.069(10), 2.031(2), and 2.023(5) Å for X = Cl,[14] F,[10] ONO, and NO_2,[3] respectively). A relatively strong coordination of amino nitrogen

---

[36] The reaction of $[Cu(H_2O)(Me_ntpa)]^{2+}$ ($n = 0, 1, 2, 3$) with NO_2^- is rapid, because greenish blue color of $[Cu(H_2O)(Me_ntpa)]^{2+}$ rapidly changed to green by the addition of $NaNO_2$.

[37] Addison, A. W.; Rao, T. N.; Reedijk, J.; Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg)

$[Cu(H_2O)(tpa)](ClO_4)_2$ (**1**)			
Cu−O1	1.980(5)	Cu−N1	1.941(6)
Cu−N2	2.054(6)	Cu−N3	2.038(7)
Cu−N4	2.069(6)		
O1−Cu−N1	177.8(2)	O1−Cu−N2	94.5(2)
O1−Cu−N3	98.9(2)	O1−Cu−N4	99.4(2)
N1−Cu−N2	83.4(2)	N1−Cu−N3	81.7(3)
N1−Cu−N4	82.1(2)	N2−Cu−N3	119.9(2)
N2−Cu−N4	118.2(3)	N3−Cu−N4	116.8(2)
$[CuCl(Me_1tpa)]ClO_4$ (**2**)			
Cu1−Cl1	2.251(3)	Cu1−N1	2.057(8)
Cu1−N2	1.988(8)	Cu1−N3	1.990(8)
Cu1−N4	2.337(8)	Cu2−Cl2	2.247(3)
Cu2−N5	2.038(8)	Cu2−N6	1.966(9)
Cu2−N7	1.975(8)	Cu2−N8	2.581(8)
Cl1−Cu1−N1	169.3(2)	Cl1−Cu1−N2	97.0(3)
Cl1−Cu1−N3	95.6(3)	Cl1−Cu1−N4	110.6(2)
N1−Cu1−N2	83.5(3)	N1−Cu1−N3	81.2(3)
N1−Cu1−N4	80.1(3)	N2−Cu1−N3	159.8(3)
N2−Cu1−N4	86.5(3)	N3−Cu1−N4	103.7(3)
Cl2−Cu2−N5	177.9(3)	Cl2−Cu2−N6	97.1(3)
Cl2−Cu2−N7	97.7(3)	Cl2−Cu2−N8	103.3(2)
N5−Cu2−N6	84.0(4)	N5−Cu2−N7	81.0(3)
N5−Cu2−N8	78.6(3)	N6−Cu2−N7	163.6(4)
N6−Cu2−N8	83.5(3)	N7−Cu2−N8	99.8(3)
$[CuCl(Me_2tpa)]ClO_4$ (**3**)			
Cu−Cl	2.253(4)	Cu−N1	2.064(9)
Cu−N2	1.98(1)	Cu−N3	2.02(1)
Cu−N4	2.27(1)		
Cl−Cu−N1	163.5(3)	Cl−Cu−N2	93.4(3)
Cl−Cu−N3	99.6(3)	Cl−Cu−N4	115.4(3)
N1−Cu−N2	83.4(4)	N1−Cu−N3	79.5(4)
N1−Cu−N4	80.8(4)	N2−Cu−N3	159.3(4)
N2−Cu−N4	89.6(4)	N3−Cu−N4	99.1(4)
$[CuCl(Me_3tpa)][CuCl_2(Me_3tpa)]ClO_4$ (**5**)			
Cu1−Cl1	2.240(2)	Cu1−N1	2.092(6)
Cu1−N2	2.047(7)	Cu1−N3	2.035(7)
Cu1−N4	2.161(6)		
Cu2−Cl2	2.292(2)	Cu2−Cl3	2.373(2)
Cu2−N5	2.145(6)	Cu2−N6	2.014(6)
Cu2−N7	2.017(6)		
Cl1−Cu1−N1	135.3(2)	Cl1−Cu1−N2	94.3(2)
Cl1−Cu1−N3	96.0(2)	Cl1−Cu1−N4	140.8(2)
N1−Cu1−N2	80.6(3)	N1−Cu1−N3	80.9(3)
N1−Cu1−N4	83.9(2)	N2−Cu1−N3	161.0(3)
N2−Cu1−N4	92.4(3)	N3−Cu1−N4	89.6(3)
Cl2−Cu2−Cl3	131.4(1)	Cl2−Cu2−N5	123.3(2)
Cl2−Cu2−N6	95.9(2)	Cl2−Cu2−N7	90.6(2)
Cl3−Cu2−N5	105.1(2)	Cl3−Cu2−N6	93.9(2)
Cl3−Cu2−N7	93.4(2)	N5−Cu2−N6	81.2(2)
N5−Cu2−N7	82.2(2)	N6−Cu2−N7	163.1(2)

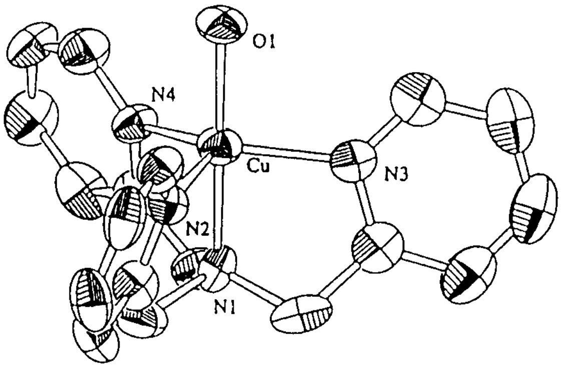

Figure 2. Molecular structure of $[Cu(H_2O)(tpa)]^{2+}$ (**1**) with atom labeling. Carbon atoms are not labeled and hydrogen atoms are omitted for clarity.

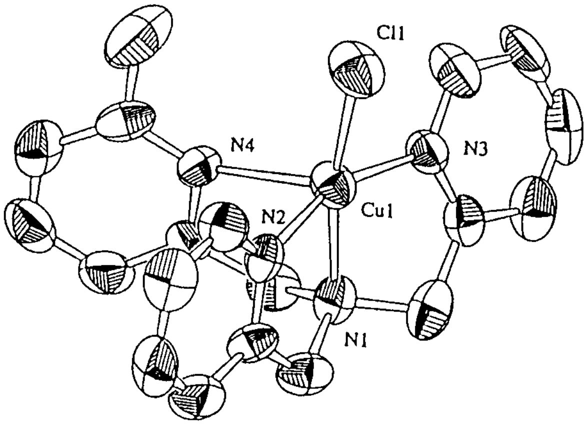

Figure 3. Molecular structure of $[CuCl(Me_1tpa)]^+$ (**2**) with atom labeling. Carbon atoms are not labeled and hydrogen atoms are omitted for clarity.

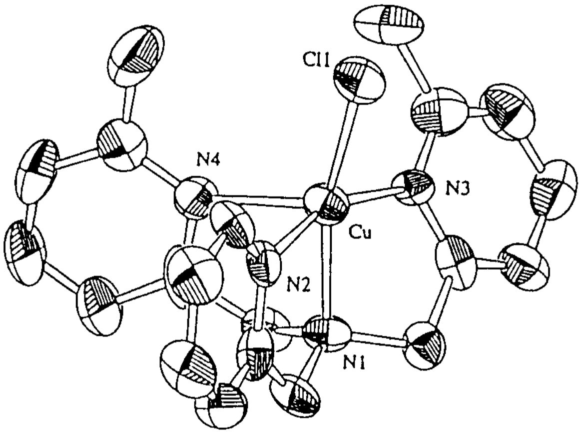

Figure 4. Molecular structure of $[CuCl(Me_2tpa)]^+$ (**3**) with atom labeling. Carbon atoms are not labeled and hydrogen atoms are omitted for clarity.

to Cu^{2+} of **1** may be associated with an elongation of the *trans* Cu−OH_2 bond distance (1.980(5) Å) compared with the Cu−ONO distance of $[Cu(ONO)(tpa)]^+$ (1.938(2) Å).

Blue $[CuCl(Me_1tpa)]ClO_4$ (**2**) crystallized in the triclinic system, $P\bar{1}$, and $Z = 4$. In the unit cell, therefore, two independent molecules (Cu1 and Cu2) exist and showed slightly different geometries with each other. The geometries of the cationic units of **2** were distorted square pyramid ($\tau = 0.16$ and 0.24), in which two pyridyl nitrogen atoms, one amino nitrogen, and chloride atom form the basal plane, and the 6-methylpyridyl ligand is located in the axial position (Figure 3). The Cu−N_{py} bond distances in the basal plane (1.988(8) and 1.990(8) Å for the Cu1 unit and 1.966(9) and 1.975(8) Å for the Cu2 unit) are shortened compared with those of **1** (2.054(6), 2.038(7) Å), while the Cu−N_{py} bond distances at the axial position (2.337(8) and 2.581(8) Å) of **2** are substantially elongated compared with the Cu−N_{py} bond distances in the basal plane (Figure 6). Shortening of the bond distances in the basal plane (Cu−N_{amino}, Cu−N_{py}, and Cu−Cl) and lengthening of the axial bond length (Cu−N_{py}) are commonly observed in square pyramidal copper(II) complexes.

The geometry of **3** is slightly distorted square pyramid as similar to **2**, and Cl, N1, N2, and N3 atoms form a basal plane with an axial Cu−N4 bond ($\tau = 0.07$) (Figure 4). Despite the ligation of the 6-methylpyridyl nitrogen (N3) to Cu^{2+} in the basal plane, the Cu−N and Cu−Cl bond distances in the equatorial plane of **3** are close to those of **2**. The Cu−N bond distances of **3** are in the following order: Cu−N2 (pyridyl in the basal plane) < Cu−N3 (6-methylpyridyl in the basal plane) < Cu−N1 (amino nitrogen in the basal plane) < Cu−N4 (6-

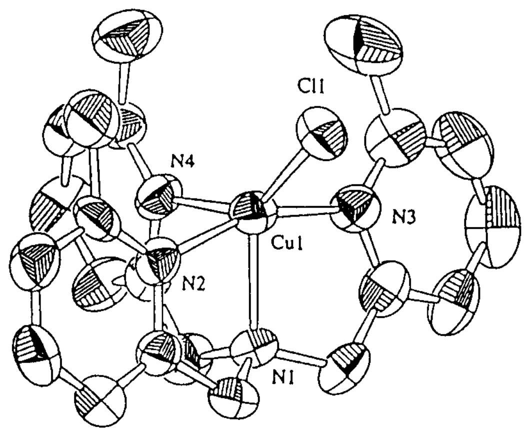

Figure 5. Molecular structure of $[CuCl(Me_3tpa)]^+$ with atom labeling. Carbon atoms are not labeled and hydrogen atoms are omitted for clarity.

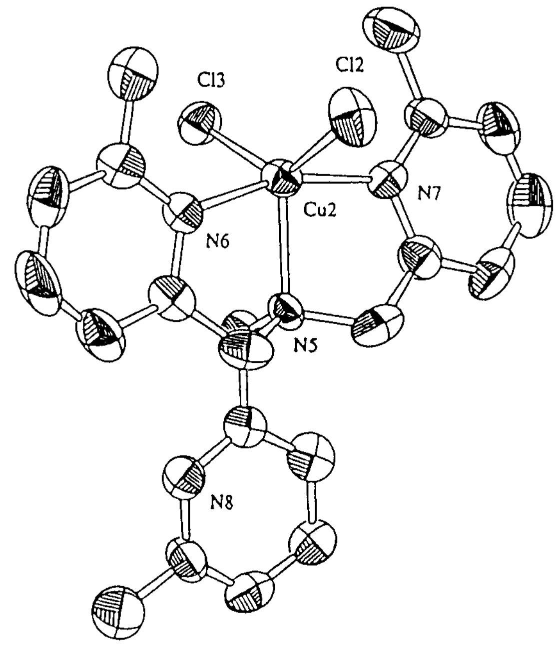

Figure 6. Molecular structure of $[CuCl_2(Me_3tpa)]$ with atom labeling. Carbon atoms are not labeled and hydrogen atoms are omitted for clarity.

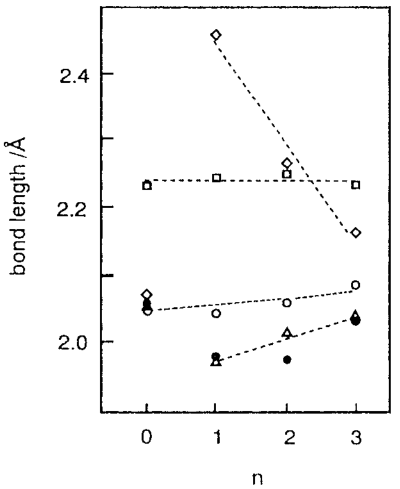

Figure 7. The relevant bond lengths of $[CuCl(Me_ntpa)]^+$ ($n = 0, 1, 2, 3$); Cl (□), N1 (○), N2 (●), N3 (△), and N4 (◇).

Table 4. Summary of Coordination Geometry Parameters

formula	no.	β/deg	α/deg	τ	type
$[Cu(H_2O)(tpa)]^{2+}$	**1**	177.8	119.9	0.97	trigonal bipyramidal
$[CuCl(Me_1tpa)]^{+\,a}$	**2**	169.3	159.8	0.16	square pyramidal
		177.9	163.6	0.24	square pyramidal
$[CuCl(Me_2tpa)]^+$	**3**	163.5	159.3	0.07	square pyramidal
$[CuCl(Me_3tpa)]^{+\,b}$	**4**	161.0	135.3	0.43	intermediate
$[CuCl_2(Me_3tpa)]$		163.1	131.4	0.53	intermediate

[a] There are two independent molecules in the unit cell. [b] The formula of complex **4** is $[CuCl(Me_3tpa)][CuCl_2(Me_3tpa)]ClO_4$.

methylpyridyl in the axial bond). The fact that the Cu−N3 (6-methylpyridyl) bond distance (2.02(1) Å) is close to the Cu−N2 (pyridyl) one (1.98(1) Å) suggests that 6-methylpyridyl nitrogen in the equatorial plane is linked to Cu^{2+} in the square pyramid geometry without a serious steric hindrance.

For $[CuCl(Me_3tpa)][CuCl_2(Me_3tpa)]^+$ (**4**), two different Cu(II) complexes (cationic Cu1 and neutral Cu2) exist in the unit cell; one is $[CuCl(Me_3tpa)]^+$ and the other is $[CuCl_2(Me_3tpa)]$. The geometries of these complexes were intermediate between trigonal bipyramid and square pyramid ($\tau = 0.43$ and 0.53 for the Cu1 and Cu2 complexes). In $[CuCl(Me_3tpa)]^+$, a basal plane is formed by a chloride atom (Cl1), an amino nitrogen atom (N1), and two pyridyl nitrogen atoms (N2 and N3) (Figure 5). Although the Cu−N bond distances in the basal plane (Cu1−N1, Cu1−N2, and Cu1−N3) are slightly longer than those of **2** and **3**, not only the Cu1−Cl1 but also the Cu1−N2 and Cu1−N3 bond distances in $[CuCl(Me_3tpa)]^+$ are almost same as those in $[CuCl(tpa)]^+$ (Figure 7). For $[CuCl_2(Me_3tpa)]$, the Cl2−Cu2−Cl3 (131.4(1)°), Cl2−Cu2−N5 (123.3(2)°), and Cl3−Cu2−N5 (105.1(2)°) bond angles revealed that these atoms form an almost regular triangle plane in the equatorial plane (Figure 6). The Cu2−Cl2 (2.292(2) Å) and Cu2−Cl3 (2.373(2) Å) bond distances in $[CuCl_2(Me_3tpa)]$ are longer than the Cu1−Cl1 one (2.239(2) Å) in $[CuCl(Me_3tpa)]^+$. The two axial bonds between 6-methylpyridyl nitrogen atoms (N6 and N7) and Cu2 are 2.014(6) and 2.017(6) Å, which are substantially shrunken compared with the axial Cu1−N4 bond length (2.161(6) Å).

Relationship between Structures and Electrochemical Behavior. The Cu−Cl and the Cu−N1 (amino nitrogen) bond distances of $[CuCl(Me_ntpa)]^+$ ($n = 0, 1, 2, 3$) are almost constant, while the $Cu-N_{py}$ bond distances are largely dependent on the Me_ntpa ligands (Figure 7). The bond distances between Cu^{2+} and 6-methylpyridyl nitrogen atoms in $[CuCl(Me_1tpa)]^+$ and $[CuCl(Me_2tpa)]^+$ are longer than the remaining $Cu-N_{py}$ bonds (Figure 7). The Cu−N4 bond distances of $[CuCl(Me_ntpa)]^+$ ($n = 1, 2, 3$), however, have shrunk with an increase in the number of methyl groups (Figure 7), suggesting that $[CuCl(Me_3tpa)]^{2+}$ is not necessarily a sterically hindered complex compared with $[CuCl(Me_2tpa)]^+$ and $[CuCl(Metpa)]^+$. The redox potentials of Cu(II)/Cu(I) couples have been discussed in terms of the thermal stability of the Cu(I) state and hydrophobicity of the ligands.[2,4,6,8,13,17,19,21,25] The $E_{1/2}$ values of the Cu(II)/Cu(I) redox couples shift to positive potentials in the order tpa < Me_1tpa < Me_2tpa < Me_3tpa complexes. These Cu(II) complexes have various structures such as trigonal bipyramidal, square pyramidal, and an intermediate between them. The redox potentials of the Cu(II)/Cu(I) couples in the present study, therefore, may be primarily controlled by the molecular structures rather than hydrophobicity of the complexes. Furthermore, redox reactions of the present Cu(II) complexes are likely to be accompanied by configurational changes, since copper(I) complexes with tripodal ligands such as $[Cu(CH_3CN)(tpa)]^+$,[9] $[Cu(tepa)]^+$,[15] $[Cu(CH_3CN)(tppa)]^+$, $[Cu(tppa)]^+$,[2] and $[Cu(tmqa)]$ [8] are trigonal bipyramidal or tetrahedral structures. The pentagonal trigonal bipyramid structures of $[Cu(H_2O)(tpa)]^{2+}$ and $[CuX(tpa)]^+$ (X = F, Cl, ONO, NO_2) probably are retained in their Cu(I) states from the analogy to the trigonal bipyramidal $[Cu(CH_3CN)(tpa)]^+$.[9] En-

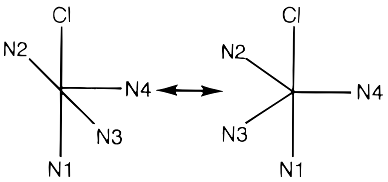

Figure 8. Structural change between square pyramid and trigonal bipyramid.

ergy barriers for configurational changes of metal complexes with tripodal ligands would be higher than those with monodentate ligands. The quasi-reversible $[Cu(H_2O)(Me_ntpa)]^{2+/+}$ (n = 1, 2, 3) redox couples, therefore, presumably result from the configurational changes between square pyramidal or distorted square pyramidal Cu(II) complexes and trigonal bipyramidal or tetrahedral Cu(I) ones. Figure 8 shows the most reasonable path for the configurational changes between square pyramid and trigonal bipyramid.[25] Such a process may be largely influenced by the N1−Cu−Cl and N2−Cu−N3 bond angles and the position of Cu. The N1−Cu−Cl and N2−Cu−N3 bond angles and the distances of Cu^{2+} from the least-square plane formed by the Cl, N1, N2, and N3 atoms of $[CuCl(Me_ntpa)]^+$ (n = 1, 2, 3) are 169.3 and 159.8° and 0.22 Å for n = 1; 163.5 and 159.3° and 0.28 Å for n = 2; and 135.3 and 161.0° and 0.60 Å for n = 3, respectively. The degree of the deviation of Cu(II) out of the equatorial plane has a similar tendency to decrease with the reversibility of the Cu(II)/Cu(I) couple. Taking into account that the adduct formation between $[Cu(H_2O)(Me_ntpa)]^{2+}$ (n = 0, 1, 2, 3) and NO_2^- smoothly took place, the catalytic activity of these complexes for the reduction of NO_2^- may be correlated with the rate of the electron transfer to the adducts and the redox potentials of the Cu(II)/Cu(I) couples. The present study indicates that Cu−ONO (or Cu−NO_2) adducts which undergo redox reactions without serious structural changes are suitable for functunal models of copper-containing nitrite reductases.

Acknowledgment. This research was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 07740532) from the Ministry of Education, Science and Culture.

Supporting Information Available: Tables of complete information on collected data and refinement, atomic coordinates, thermal parameters, bond lengths and angles, torsion or conformation angles, and least-squares planes and ORTEP drawings with atom labeling for complexes **1**−**4** (66 pages). Ordering information is given on any current masthead page.

IC960303N