Bull. Chem. Soc. Jpn., 71, 637—645 (1998)

Preparations, Structures, and Properties of Cu(II) Complexes with Tripodal Tetradentate Ligand, Tris(6-pivaloylamino-2-pyridylmethyl)amine (Htppa), and Reaction of Its Cu(I) Complex with Dioxygen

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(Received September 22, 1997)

Mononuclear copper complexes with a tripodal tetradentate ligand, tris(6-pivaloylamino-2-pyridylmethyl)amine (Htppa), and several anions have been prepared as a model metal centre of copper enzymes, whose structures have been examined by electronic absorption, ESR and NMR spectral, cyclic voltammetry, and X-ray diffraction methods. Those with an anion such as OH^-, Cl^-, Br^-, and I^- were shown to form a trigonal-bipyramidal geometry. The X-ray structures of $[Cu(Htppa)](ClO_4)_2 \cdot 2H_2O \cdot CH_3OH$, $[CuCl(Htppa)]ClO_4$, $[Cu(OH)(Htppa)]ClO_4$, $[Cu(OH)(tppa)]$, and $[Cu(tppa)](BPh_4)$, obtained as a single crystal, revealed all trigonal-bipyramidal geometry with four nitrogen atoms of Htppa in trigonal plane and axial position and with the anion in another apical position. The reaction with NaN_3 gave $[Cu(N_3)_2(Htppa)]$, whose crystal structure was a square-pyramid with three nitrogen atoms of Htppa and N_3^- in square-planar positions and with another N_3^- in apical position. The redox potentials of $[CuCl(Htppa)]ClO_4$ in MeCN or CH_2Cl_2 showed almost reversible Cu^I/Cu^{II} couples at 0.225 and 0.300 V vs. Ag/AgCl, respectively, which are characteristically high for the usual copper complexes. The addition of dioxygen to the Cu(I)–Htppa complex prepared from $[Cu(MeCN)_4]ClO_4$ and Htppa (1 : 1) in methanol solution at -78 °C resulted in an immediate absorption spectral change, with two well-separated absorptions at 657 ($\varepsilon = 110\ M^{-1}\ cm^{-1}$) and 803 nm ($\varepsilon = 120\ M^{-1}\ cm^{-1}$) and an intense band at 315 nm ($\varepsilon =$ ca. $4000\ M^{-1}\ cm^{-1}$) as a shoulder. Simultaneous ESR experiments of the same complex solution exhibited a silent spectrum, and the NMR spectrum at -80 °C was diamagnetic. These facts indicate the formation of $Cu^{II}–O_2^-$ species. Interestingly, the CO gas bubbling into a $CH_3OH/THF/EtCN$ (4 : 3 : 3) solution of the superoxo complex species at -78 °C led to a significant color change from yellow-green to pale yellow, and alternate bubblings of O_2 and CO to the solution exhibited a reversible spectral change with an isosbestic point at 521 nm due to the reversible formation of the $Cu^{II}–O_2^-$ species.

The chemistry of copper dioxygen complexes has advanced considerably in the last 10 years.[1] Appropriate ligands such as tripodal ones have frequently been designed and used in bioinorganic studies, as they form coordination structures similar to the active site in metal enzymes and they allow tuning of the steric and electronic properties of the metal centre. Many copper complexes with such low-molecular weight ligands, which contain pyridine,[2—17] quinoline,[5,7] imidazole,[8—13] pyrazole,[11,12,15,18,19] and imidazolyl donor groups,[20] have been prepared as structural and/or functional models in copper-containing enzymes such as hemocyanin,[21,22] tyrosinase,[23] galactose oxidase,[24] amine oxidase,[25] ascorbate oxidase,[26] and superoxide dismutase.[27] Most of the interests have been focused on the binding and the activation of dioxygen. In order to construct new types of binding and activating models of dioxygen molecules, we have also tried to synthesize a mononuclear copper complex with a tripodal tetradentate ligand, tris{(6-pivaloylamino-2-pyridyl)methyl}amine (Htppa) (Chart 1).[28,29] This novel ligand has four characteristic functional groups, i.e., four coordination sites for metal ion, three NH groups for hydrogen bonds to fix a small molecule such as dioxygen, three hydrophobic groups to protect the small bound molecule and to prevent dinucleation of coordinated metal centers, and electron-withdrawing pivaloylamino groups to stabilize the lower valence state of copper.

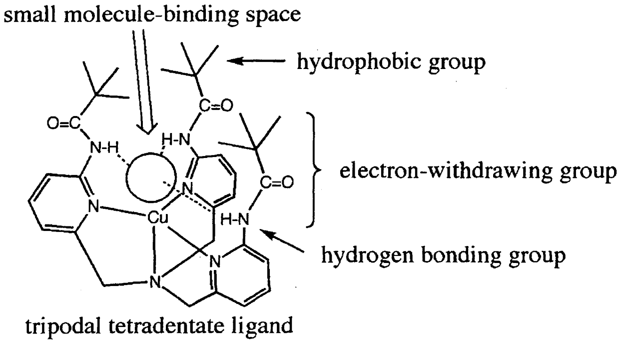

Chart 1.

Here, we describe the binding ability of the Cu^{II}–Htppa complex for a small substrate and the reaction of the Cu^I–Htppa complex with a dioxygen molecule. Previously, the characterization of $Cu^{II}–O_2^-$ species obtained in the reaction of the Cu^I–Htppa complex with dioxygen has been reported by us as a communication,[28] but some questions were recently raised.[30] We present also here the details of its characterization.

Experimental

Materials and Measurements. Reagents and solvents employed were of the highest grade available. All solvents for spectroscopies were purified by further distillation before use. Other chemicals were used without further purification.

Electronic absorption spectra were taken at −78 °C on a JASCO UVIDEC-660 spectrophotometer equipped with a San-ei Giken low temperature cell. X-Band ESR spectra of frozen solution were recorded at 77 K by using a JEOL RE-1X ESR spectrometer. ^{1}H NMR spectra were measured on a Varian VXR-300S or JEOL Lambda-500 spectrometer with TMS as an internal standard. Positive-ion FAB mass spectra were obtained with a Shimadzu KRATOS CONCEPT I S mass spectrometers. Cyclic voltammetric measurements were performed using a Bioanalytical Systems (BAS) CV-27 Voltammograph equipped with a Graphtec X–Y WX2400 chart recorder. A 3-mm diameter glassy-carbon working electrode, an Ag/AgCl reference electrode, and a Pt-wire counter electrode were used in a glass cell having a working compartment (approximately 3-mL in volume). All measurements were made at 25 °C under an argon atmosphere in solution with tetra(*n*-butyl)ammonium tetrafluoroborate (0.1 M, $1\ \mathrm{M}=1\ \mathrm{mol\,dm^{-3}}$) as a supporting electrolyte at a scan rate of $100\ \mathrm{mV\,s^{-1}}$. Electrochemical potentials were reported vs. the normal hydrogen electrode (NHE) by addition of 222 mV.[34]

Synthesis of Ligand: Htppa. The ligand Htppa was synthesized as previously described.[29]

Preparation of [Cu(Htppa)]$(ClO_4)_2\cdot 2H_2O\cdot CH_3OH$. To a stirred acetone solution (5 mL) of $Cu(ClO_4)_2\cdot 6H_2O$ (185 mg, 0.5 mmol) was added Htppa (294 mg, 0.5 mmol). The blue precipitate which formed immediately was filtered off, and was recrystallized from acetone–methanol–water (2 : 1 : 3) to give 449 mg (96%). This complex solution, on standing at room temperature, gave single crystals suitable for X-ray structure analysis. Anal. Calcd for $CuC_{33}H_{45}N_7O_3\cdot 2ClO_4\cdot H_2O$: C, 45.65; H, 5.456; N, 11.29%. Found: C, 45.79; H, 5.198; N, 11.27%. Positive ion FAB mass spectrum: *m/z* 650 ($[Cu(C_{33}H_{44}N_7O_3)]^+$).

Preparation of [Cu(tppa)](BPh_4). To a stirred MeCN solution (5 mL) of $[Cu(MeCN)_4]ClO_4$ (164 mg, 0.5 mmol) was added Htppa (294 mg, 0.5 mmol). The perchlorate anion was exchanged by addition of $NaBPh_4$ (342 mg, 1 mmol) to the solution. The green precipitate which formed immediately was filtered off, and was recrystallized from MeCN solution to give 441 mg (91%). This complex solution, on standing in a refrigerator, gave single crystals suitable for X-ray structure analysis.

Preparation of [Cu(OH)(tppa)]$\cdot 2H_2O\cdot CH_3COCH_3$. To an acetone solution (5 mL, 30 mM) of [Cu(Htppa)]$(ClO_4)_2\cdot H_2O$ (130 mg, 0.15 mmol) was added NaOH (13.2 mg, 0.33 mmol). The green precipitate which formed immediately was filtered off, and was recrystallized from acetone–methanol–water (2 : 1 : 3) to give 101 mg (93%). This complex solution, on standing at room temperature, gave single crystals suitable for X-ray structure analysis. Anal. Calcd for $CuC_{33}H_{44}N_7O_3\cdot OH\cdot 3H_2O$: C, 54.95; H, 7.126; N, 13.59%. Found: C, 54.96; H, 6.894; N, 13.46%.

Preparation of [Cu$(N_3)_2$(Htppa)]. To a THF solution (5 mL, 20 mM) of [Cu(Htppa)]$(ClO_4)_2\cdot H_2O$ (86.8 mg, 0.10 mmol) was added NaN_3 (14.3 mg, 0.22 mmol). The dark-green precipitate which formed immediately was filtered off, and was recrystallized from THF–water (1 : 1) to give 75 mg (97%). This complex solution, on standing at room temperature, gave blue single crystals suitable for X-ray structure analysis. The Cu–Htppa–N_3^- system was not obtained as a single crystal from the MeCN solution containing [Cu(Htppa)]$(ClO_4)_2\cdot H_2O$ and NaN_3 with 1 : 1 molar ratio.

Preparation of [Cu$(NO_2)_2$(Htppa)]. To an MeCN solution (5 mL, 20 mM) of [Cu(Htppa)]$(ClO_4)_2\cdot H_2O$ (86.8 mg, 0.10 mmol) was added $NaNO_2$ (15.2 mg, 0.22 mmol). The blue precipitate which formed immediately was filtered off, and was recrystallized from MeCN–water (1 : 1) to give 64 mg (86%). This complex solution, on standing at room temperature, gave single crystals suitable for X-ray structure analysis. The Cu–Htppa–NO_2^- system was not obtained as a single crystal from the MeCN solution containing [Cu(Htppa)]$(ClO_4)_2\cdot H_2O$ and $NaNO_2$ with 1 : 1 molar ratio.

Preparations of $[Cu(X)(Htppa)]^+$ ($X=Br^-, I^-$). The preparation of $[Cu(Htppa)Br]^+$ was carried out by the addition of NaBr (1.5 mg, 0.015 mmol) to an MeCN (5 mL, 3.00 mM) solution of [Cu(Htppa)]$(ClO_4)_2\cdot H_2O$ (13.0 mg, 0.015 mmol). That of $[Cu(Htppa)I]^+$ was performed by the addition of NaI (2.4 mg, 0.015 mmol) to a THF solution (5 mL, 3.00 mM) solution of [Cu(Htppa)]$(ClO_4)_2\cdot H_2O$ (13.0 mg, 0.015 mmol). The formations of $[Cu(X)(Htppa)]^+$ were confirmed by absorption spectral changes.

Reaction of [Cu(Htppa)]ClO_4 with Dioxygen. To an MeCN solution (5 mL, 3 mM) of $[Cu(MeCN)_4](ClO_4)$ (4.91 mg, 0.015 mmol) under thorough bubbling with Ar was added Htppa (8.82 mg, 0.015 mmol) at r.t., which was used for the reaction with dioxygen. The preparations in MeOH and THF were performed by the same procedure as for MeCN, and that in CH_2Cl_2, was carried out in 1 mM scale because of its poor solubility.

Reversible Binding of O_2 to [Cu(Htppa)]ClO_4. To a MeOH/THF/EtCN mixed solvent (4 : 3 : 3) volume ratio, 1 mL, 10 mM) of $[Cu(MeCN)_4](ClO_4)$ (5.59 mg, 0.32 mmol) under thorough bubbling with Ar was added Htppa (7.99 mg, 0.32 mmol), which was used for the alternate reactions with O_2 and CO gas. The absorption spectroscopy was performed at −78 °C.

X-Ray Structure Analyses of [Cu(Htppa)]$(ClO_4)_2\cdot 2H_2O\cdot CH_3OH$, [Cu(OH)(Htppa)]$\cdot 2H_2O\cdot CH_3COCH_3$, [Cu(tppa)]$BPh_4$, [Cu$(N_3)_2$(Htppa)]$\cdot 2H_2O$, and [Cu$(NO_2)_2$(Htppa)]. Each of the crystals of these complexes suitable for X-ray diffraction measurements was mounted on a glass capillary. The diffraction data were collected with graphite-monochromated Mo $K\alpha$ radiation on an Enraf–Nonius CAD4-EXPRESS four-circle diffractometer at room temperature with the ω–2θ scan technique. Crystal data and experimental details are listed in Table 1.

All the structures were solved by a combination of direct method and Fourier techniques; the structures were anisotropically refined for non-hydrogen atoms by full-matrix least-squares calculations. Refinements were continued until all shifts were smaller than one-third of the standard deviations of the parameters involved. Atomic scattering factors and anomalous dispersion terms were taken from International Tables for X-Ray Crystallography.[31] Empirical absorption corrections using Ψ-scan were applied for all crystals after a full isotropic refinement of non-hydrogen atoms. Since the reflection data were not enough to refine all the parameters containing the hydrogen atoms, they were not included for further refinement; their positions were determined from difference Fourier maps, except for a part of hydrogen atoms. All the calculations were carried out on a micro VAX 3100 computer by using the MolEN program.[32] Tables of the atomic coordinates, thermal parameters, bond lengths and angles, torsion angles, and observed and calculated structure factors for the complexes have been deposited as Document No. 71016 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Table 1. Crystallographic Data and Experimental Details for $[Cu(Htppa)](ClO_4)_2 \cdot 2H_2O \cdot CH_3OH$, $[Cu(OH)(tppa)] \cdot 2H_2O \cdot CH_3COCH_3$, $[Cu(tppa)]B(C_6H_5)_4$, $[Cu(N_3)_2(Htppa)] \cdot 2H_2O$, and $[Cu(NO_2)_2(Htppa)]$

	$[Cu(Htppa)](ClO_4)_2$ $\cdot 2H_2O \cdot CH_3OH$	$[Cu(OH)(tppa)]$ $\cdot 2H_2O \cdot CH_3COCH_3$	$[Cu(tppa)]B(C_6H_5)_4$	$[Cu(N_3)_2(Htppa)]$ $\cdot 2H_2O$	$[Cu(NO_2)_2(Htppa)]$
Formula	$C_{34}H_{53}N_7O_{14}CuCl_2$	$C_{36}H_{55}N_7O_7Cu$	$C_{57}H_{64}N_7O_3BCu$	$C_{33}H_{49}N_{13}O_5Cu$	$C_{33}H_{45}N_9O_7Cu$
F.W.	936.30	761.42	969.54	771.38	743.32
Color	Blue	Green	Green	Dark green	Green
Crystal dimensions/mm	0.3 × 0.3 × 0.4	0.1 × 0.3 × 0.7	0.25 × 0.25 × 0.3	0.1 × 0.5 × 0.5	0.15 × 0.3 × 0.4
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	Cc (#9)	$P2_1/n$ (#14)	$P2_12_12_1$ (#19)
a/Å	10.063(1)	10.193(2)	22.917(2)	15.802(2)	9.2601(9)
b/Å	11.452(2)	13.594(4)	14.493(1)	17.462(2)	12.592(1)
c/Å	20.518(4)	15.886(4)	20.423(2)	17.110(2)	30.932(3)
α/deg	92.92(2)	107.48(2)	—	—	—
β/deg	91.30(1)	99.82(2)	121.417(8)	114.782(9)	—
γ/deg	107.26(1)	98.03(2)	—	—	—
V/Å^3	2253.6(7)	2026(1)	5788.8(9)	4287(1)	3598.2(2)
D_{calcd}/g cm^{-3}	1.385	1.249	1.107	1.195	1.372
Z	2	2	4	4	4
F(000)	962	810	2052	1628	1564
μ(Mo $K\alpha$)/cm^{-1}	6.735	5.892	4.179	5.580	6.631
Radiation	Graphite monochromated Mo $K\alpha$ (λ = 0.71073 Å)				
T/°C	21	21	21	21	21
$2\theta_{max}$/deg	52.64	48.62	52.64	52.64	52.64
No. of reflections measured	9655	6972	6298	9302	4141
No. of reflections used [$I > 3.00\sigma(I)$]	4434	1944	3241	2882	1958
No. of variables	713	461	877	662	452
R;R_w [a]	0.109; 0.124	0.058; 0.058	0.066; 0.077	0.071; 0.080	0.055; 0.056

a) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 4F_o^2/\sigma^2(F_o)^2$.

Results and Discussion

Reactions of $[Cu(Htppa)](ClO_4)_2$ with Small Anions as Examined by Electronic Absorption Spectra. The electronic absorption spectral data of samples obtained by reactions of $[Cu(Htppa)](ClO_4)_2$ with small anions such as Cl^-, Br^-, I^-, OH^-, N_3^-, and NO_2^- at 1 : 1 and/or 1 : 2 molar ratio in MeCN or THF solution were listed in Table 2. The complex solutions showed well-separated d–d bands in the wavelength range 600—1000 nm, except for a few complexes. Those complexes with Cl^-, Br^-, I^-, and OH^- suggested the spectral patterns characteristic of a trigonal-bipyramidal geometry.[33] They also exhibited weak absorption bands assignable to LMCT at 380—460 nm except for the complex with I^-. That with I^- showed an intense band at 445 nm (ε = 2000 M^{-1} cm^{-1}). These facts suggest that the Cu(II) complex can bind small external ligands to the axial position of the metal complex with the tripodal tetradentate ligand, Htppa. On the other hand, the reactions with N_3^- or NO_2^- demonstrated a tendency to form not only 1 : 1 but also 1 : 2 complexes, whose spectral patterns are in accord with those of a square-planar or square-pyramidal geometry.[33]

Crystal Structures of $[Cu(Htppa)](ClO_4)_2 \cdot 2H_2O \cdot CH_3OH$, $[Cu(OH)(Htppa)] \cdot 2H_2O \cdot CH_3COCH_3$, $[Cu(tppa)]BPh_4$, $[Cu(N_3)_2(Htppa)] \cdot 2H_2O$, and $[Cu(NO_2)_2(Htppa)]$. The crystal structures of $[CuCl(Htppa)]ClO_4$ and [Cu-

Table 2. Electronic Absorption Spectral Data for $[Cu(X)(Htppa)]^+$ Complexes

Complex/Solvent	LMCT (nm)/ε (M^{-1} cm^{-1})	d–d (nm)/ε (M^{-1} cm^{-1})
$[Cu(Htppa)](ClO_4^-)_2$/MeCN	380 (200)	685 (149), 775 (170)
$[CuCl(Htppa)](ClO_4^-)$/MeCN [a]	426 (110)	745 (140), 897 (207)
$[CuBr(Htppa)]^+$ [b]/MeCN	— [d]	780 (174), 870 (200)
$[CuI(Htppa)]^+$ [b]/THF	440 (2000)	676 (300), 824 (336)
$[Cu(OH)(Htppa)](ClO_4^-)$/MeCN [c]	455 (50)	678 (120), 822 (170)
$[Cu(OH)(tppa)]$/MeCN	500 (190)	660 (190), 813 (180)
$[Cu(tppa)](BPh_4^-)$/EtCN	430 (46)	735 (39), 630 (32)
$[Cu(N_3)(Htppa)]^+$ [b]/THF	430 (170)	636 (178)
$[Cu(N_3)_2(Htppa)]$/THF	400 (2820)	700 (271)
$[Cu(NO_2)(Htppa)]^+$ [b]/MeCN	450 (160)	630 (140), 733 (181)
$[Cu(NO_2)_2(Htppa)]$/MeCN	420 (300)	650 (125), 747 (170)

a) Ref. 29. b) Not isolated. c) Ref. 36. d) Not observed.

(OH)(Htppa)]ClO$_4$ have already been documented in the literature,[29,36] and all the geometries around the Cu(II) ions revealed a trigonal-bipyramidal structure, as were speculated from the above-mentioned solution structures. The crystal structures of $[Cu(Htppa)](ClO_4)_2\cdot 2H_2O\cdot CH_3OH$, $[Cu(OH)(tppa)]\cdot 2H_2O\cdot CH_3COCH_3$, and $[Cu(tppa)]BPh_4$ established here also demonstrated that the geometries around the Cu(II) ions are all trigonal-bipyramid with the three pyridine nitrogens of Htppa in the trigonal-plane and with the tertiary amine nitrogen and a small anion in the axial positions, whose molecular structures are depicted in Figs. 1, 2, and 3, respectively. Their important bond parameters are presented in Table 3 together with those of $[CuCl(Htppa)]ClO_4$[29] and $[Cu(OH)(Htppa)]ClO_4$.[36] Interestingly, the geometries around the copper ions in $[Cu(OH)(tppa)]\cdot 2H_2O\cdot CH_3COCH_3$ and $[Cu(tppa)]BPh_4$ were almost same as those in $[Cu(OH)(Htppa)]ClO_4$ and $[Cu(Htppa)](ClO_4)_2\cdot 2H_2O\cdot CH_3OH$, although the amide N–H protons attached to the coordinating carbonyls were eliminated.

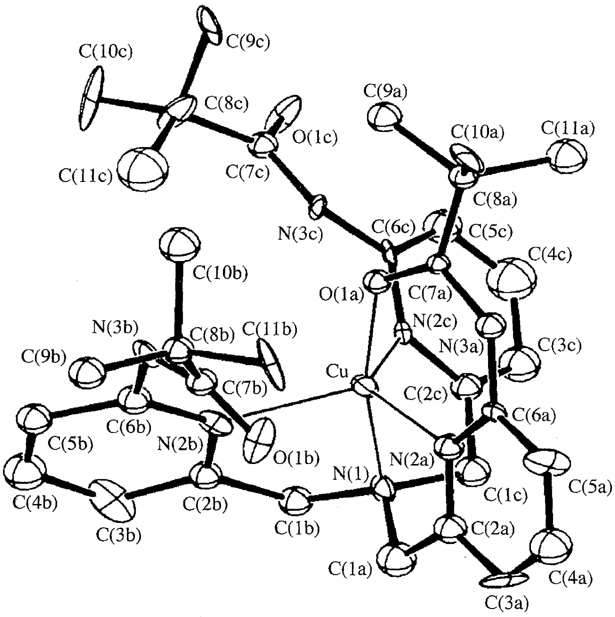

Fig. 1. ORTEP drawing of $[Cu(Htppa)]^{2+}$ with atomic labeling scheme.

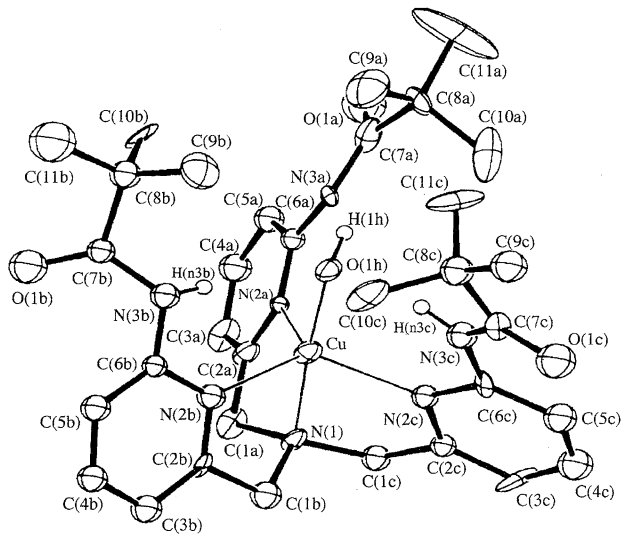

Fig. 2. ORTEP drawing of [Cu(OH)(tppa)] with atomic labeling scheme.

As were estimated from their electronic absorption spectra, the $[Cu(N_3)_2(Htppa)]\cdot 2H_2O$ and $[Cu(NO_2)_2(Htppa)]$ complexes had a square-pyramidal geometry (Figs. 4 and 5), judging from the bond parameters, which are compiled in Table 4. The metal coordination in $[Cu(N_3)_2(Htppa)]\cdot 2H_2O$ was surrounded with the pyridine and amine nitrogens of Htppa and two azide nitrogens in the equatorial positions

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[Cu(Htppa)](ClO_4)_2\cdot 2H_2O\cdot CH_3OH$, $[CuCl(Htppa)]ClO_4$, $[Cu(OH)(Htppa)]ClO_4$, $[Cu(OH)(tppa)]\cdot 2H_2O\cdot CH_3COCH_3$, and $[Cu(tppa)]B(C_6H_5)_4$

	$[Cu(Htppa)](ClO_4)_2$ $\cdot 2H_2O\cdot CH_3OH$	$[CuCl(Htppa)]ClO_4$[a]	$[Cu(OH)(Htppa)]ClO_4$[b]	$[Cu(OH)(tppa)]$ $\cdot 2H_2O\cdot CH_3OCH_3$	$[Cu(tppa)]B(C_6H_5)_4$
Cu–X	1.912(6)[c]	2.206(2)[d]	1.8599(9)[e]	1.861(5)[f]	1.931(7)[g]
Cu–N(1)	1.974(7)	1.954(5)	1.9857(9)	2.037(6)	2.000(8)
Cu–N(2a)	1.947(6)	2.152(4)	2.1169(9)	2.050(8)	2.15(1)
Cu–N(2b)	2.118(8)	2.135(4)	2.1834(9)	2.129(8)	1.986(6)
Cu–N(2c)	2.132(7)	2.316(5)	2.1733(9)	2.093(8)	2.086(8)
X–Cu–N(1)	167.8(3)[c]	174.9(2)[d]	175.59(5)[e]	175.9(3)[f]	172.1(4)[g]
X–Cu–N(2a)	91.6(3)[c]	101.4(1)[d]	99.46(4)[e]	101.3(3)[f]	106.0(3)[g]
X–Cu–N(2b)	111.0(3)[c]	101.0(1)[d]	103.90(4)[e]	99.3(3)[f]	92.6(3)[g]
X–Cu–N(2c)	95.6(3)[c]	97.2(1)[d]	96.08(4)[e]	97.3(3)[f]	97.6(3)[g]
N(1)–Cu–N(2a)	83.5(3)	80.7(2)	81.27(3)	82.8(3)	81.7(4)
N(1)–Cu–N(2b)	81.1(3)	81.4(2)	79.53(3)	79.6(3)	83.0(3)
N(1)–Cu–N(2c)	79.1(3)	77.7(2)	79.86(3)	79.8(3)	80.9(3)
N(2a)–Cu–N(2b)	119.1(3)	123.6(2)	116.10(4)	116.5(3)	109.6(3)
N(2a)–Cu–N(2c)	128.9(3)	110.8(2)	119.94(4)	118.6(3)	111.3(3)
N(2b)–Cu–N(2c)	105.1(3)	116.7(2)	115.49(4)	117.3(3)	133.0(4)

a) Ref. 29. b) Ref. 36. c) X = O(1a). d) X = Cl(1). e,f) X = O(1h). g) X = O(1b).

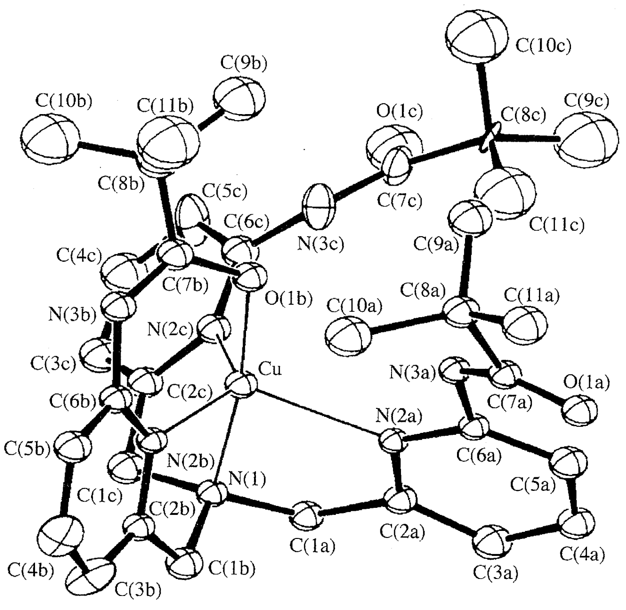

Fig. 3. ORTEP drawing of $[Cu(tppa)]^+$ with atomic labeling scheme.

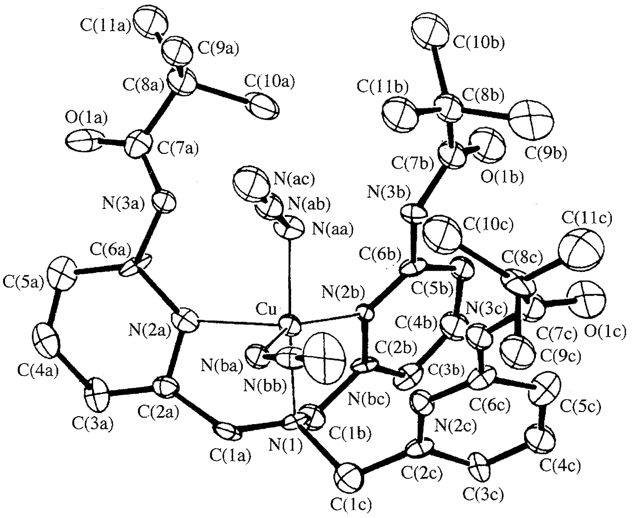

Fig. 4. ORTEP drawing of $[Cu(N_3)_2(Htppa)]$ with atomic labeling scheme.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[Cu(N_3)_2(Htppa)]\cdot 2H_2O$ and $[Cu(NO_2)_2(Htppa)]$

$[Cu(NO_2)_2(Htppa)]\cdot 2H_2O$		$[Cu(NO_2)_2(Htppa)]$	
Cu–N(aa)	1.910(8)	Cu–O(1na)	2.107(7)
Cu–N(ba)	2.013(8)	Cu–O(1nb)	2.070(7)
Cu–N(1)	2.032(8)	Cu–N(1)	2.057(7)
Cu–N(2a)	2.320(6)	Cu–N(2a)	2.051(7)
Cu–N(2b)	2.147(7)	Cu–N(2c)	2.062(7)
N(aa)–Cu–N(ba)	95.3(3)	O(1na)–Cu–O(1nb)	82.4(3)
N(aa)–Cu–N(1)	172.0(3)	O(1na)–Cu–N(1)	142.6(3)
N(aa)–Cu–N(2a)	99.1(3)	O(1na)–Cu–N(2a)	95.8(3)
N(aa)–Cu–N(2b)	93.9(3)	O(1na)–Cu–N(2c)	94.9(3)
N(ba)–Cu–N(1)	90.5(3)	O(1nb)–Cu–N(1)	134.9(3)
N(ba)–Cu–N(2a)	95.7(2)	O(1nb)–Cu–N(2a)	97.6(3)
N(ba)–Cu–N(2b)	160.3(3)	O(1nb)–Cu–N(2c)	95.4(3)
N(1)–Cu–N(2a)	74.7(3)	N(1)–Cu–N(2a)	81.4(3)
N(1)–Cu–N(2b)	82.3(3)	N(1)–Cu–N(2c)	83.0(3)
N(2a)–Cu–N(2b)	100.0(2)	N(2a)–Cu–N(2c)	164.2(3)

and with the pyridine nitrogen of Htppa in the apical position, and the remaining pyridine nitrogen was removed to be free. The coordination in $[Cu(NO_2)_2(Htppa)]$ was completed with the pyridine and amine nitrogens of Htppa and one nitro oxygen in the equatorial positions and with another nitro oxygen at the apical position, and also the remaining pyridine was removed from the central metal atom. These findings allow us to conclude that the Cu–Htppa complex can incorporate smaller anions such as Cl^-, Br^-, I^-, and OH^- into its apical position to form a trigonal-bipyramidal geometry, but that lager anions such as N_3^- and NO_2^- stabilize a square-pyramidal geometry rather than a trigonal-bipyramidal one. The larger external ligand may push out the pyridine of Htppa to spread out the narrow trigonal-bipyramidal space.

Electrochemical Properties. The cyclic voltammogram of the complex $[CuCl(Htppa)]ClO_4$ in MeCN under Ar showed a reversible one-electron redox potential at +0.225 V vs. Ag/AgCl (+0.447 V when converted to the NHE scale by the addition of +0.222 V$^{34)}$) with a pair of cathodic and anodic waves of the Cu(II)/Cu(I) couple, which are significantly higher than the $E_{1/2}$ value of the copper complexes with similar ligands, $[CuCl(tmpa)]PF_6$ (tmpa = tris{(2-pyridyl)-methyl}amine) (−0.39 V vs. NHE)$^{35)}$ and $[CuCl(bpca)]ClO_4$ (bpca = bis{(6-pivaloylamino-2-pyridyl)methyl}{(5-carboxyl-2-pyridyl)methyl}amine) (+0.241 V vs. NHE).$^{16)}$ The order of these redox potentials, i.e. tempa < bpca < Htppa complexes, may be explained in terms of the electron densities on the central metal ions. The electron-withdrawing pivaloylamino group allows the electron density on the metal ion to decrease and then the redox potential to increase. The redox potential of the Cu–Htppa complex established here is higher than the potentials given above, suggesting that the Htppa ligand will more effectively stabilize the lower oxidation state of the copper ion than the other two ligands can. The electrochemical parameters are listed in Table 5 together with those measured in CH_2Cl_2, MeOH and THF, which reveals a significant solvent-dependent redox potentials. The order of the solvent-dependent redox potentials are as follows; MeOH < THF < MeCN < CH_2Cl_2, which agrees well with that of the polarity of these solvents. And also the parameters in MeCN and CH_2Cl_2 exhibited almost reversible redox behaviours, whereas those in MeOH and THF demonstrated quasi-reversible behaviours with a large split of E_{pa} and E_{pc} (more than 100 mV).

Reaction of $[Cu^I(Htppa)]ClO_4$ with Dioxygen. As described above, the Cu–Htppa system can bind a small molecule in the trigonal-bipyramidal geometry and the Htppa ligand can stabilize the lower oxidation state of Cu, which suggests it may be suitable for reversible binding of dioxygen. Reaction of the $[Cu^I(Htppa)]ClO_4$ complex with dioxygen was performed in MeCN, MeOH, THF, and CH_2Cl_2, which was followed by electronic absorption, ESR and NMR spectra measurements. Bubbling of dioxygen into an MeCN

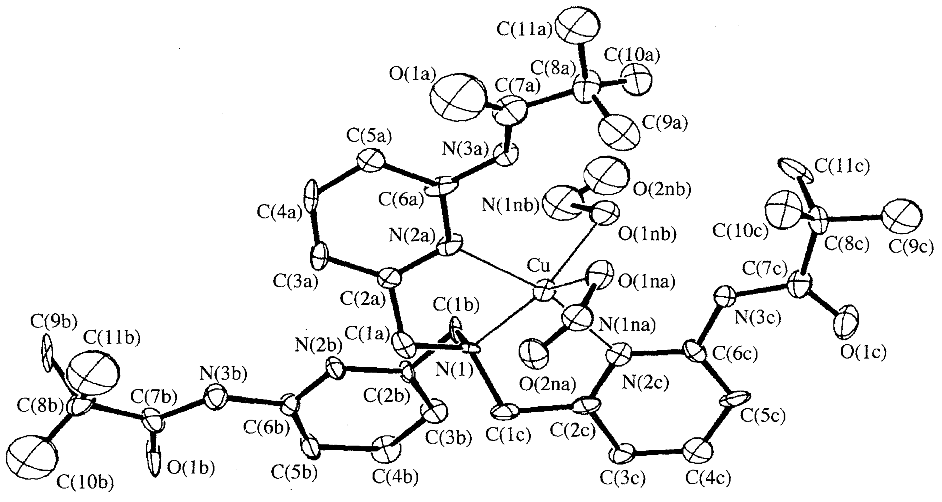

Fig. 5. ORTEP drawing of $[Cu(NO_2)_2(Htppa)]$ with atomic labeling scheme.

Table 5. Cyclic Voltammetry Data for $[CuCl(Htppa)]ClO_4$ at Room Temperature

Solvent	$E_{1/2}$[a)]/V	ΔE_p/V	i_{pa}/i_{pc}
CH_3OH	+0.030	0.350	0.68
THF	+0.124	0.603	0.79
CH_3CN	+0.225 (+0.447[b)])	0.090	0.95
CH_2Cl_2	+0.300	0.100	0.98

a) $E_{1/2} = (E_{pa}+E_{pc})/2$. b) The value is converted to the NHE scale (Ref. 34).

solution containing $[Cu^I(Htppa)]ClO_4$ at −78 °C exhibited a drastic absorption spectral change, which gave rise to new two d–d bands at 657 nm ($\varepsilon = 110$ M^{-1} cm^{-1}) and 803 nm ($\varepsilon = 117$ M^{-1} cm^{-1}) and an absorption band at 315 nm (ε = ca. 4000 M^{-1} cm^{-1}) assignable to LMCT as a shoulder peak in the vicinity of π–π* transition peaks of pyridine. The spectral pattern of the d–d bands was typical to the Cu(II) complex with a trigonal-bipyramidal geometry, as shown in Fig. 6. The LMCT band observed here may be in a higher region than the bands reported previously, $[Cu(tmpa)(O_2)]^+$ (410 nm ($\varepsilon = 4000$ M^{-1} cm^{-1}) and $[Cu(bqpa)(O_2)]^+$ (378 nm ($\varepsilon = 8200$ M^{-1} cm^{-1}) (tmpa = tris(2-pyridylmethyl)amine, bqpa = bis(2-quinolylmethyl)(2-pyridylmethyl)amine),[35] which may be explained in terms of the electronic characters of ligands. The ligand Htppa having bulky pivalamino groups weakens the coordination of the pyridine nitrogens to the copper atom, due to the steric repulsion, and then strengthens the binding of dioxygen to the metal atom due to the electroneutrality principle. This strong coordination of dioxygen to the central metal ion enlarges the d–d orbital splitting and then makes the LMCT band shift to higher energy region. The same spectral behaviours were also observed in THF and CH_2Cl_2 solutions (Fig. 6), which gave the d–d bands at 660 nm ($\varepsilon = 100$ M^{-1} cm^{-1}) and 815 nm ($\varepsilon = 125$ M^{-1} cm^{-1}) for the former and 675 nm ($\varepsilon = 100$ M^{-1} cm^{-1}) and 800 nm ($\varepsilon = 125$ M^{-1} cm^{-1}) for the latter, respectively. The reaction in THF was as fast as that in MeOH, but that in CH_2Cl_2 was quite slow. Regrettably, the explicit and characteristic LMCT bands were not observed separately in these solvents, probably because of their overlapping with the π–π* transition bands. This reaction did not proceed in MeCN at all, which means that the Cu^I complex is stabilized in MeCN, as has been well known.

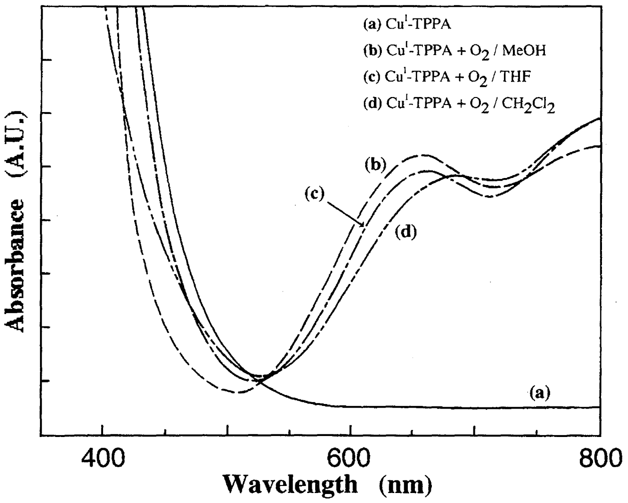

Fig. 6. Electronic absorption spectra for several solutions (MeOH, THF, CH_2Cl_2) prepared by reaction of $[Cu^I(Htppa)]ClO_4$ with dioxygen at −78 °C.

The process of reaction of $[Cu^I(Htppa)]ClO_4$ with dioxygen in MeOH was also followed by ESR measurements. The reaction of dioxygen with the Cu(I)–Htppa system prepared quite carefully demonstrated ESR silent, although its color clearly changed from pale-yellow to green. It indicates that the copper–dioxygen adduct is diamagnetic. In order to confirm the diamagnetism of the reaction solution, ^1H NMR spectra were measured in CD_3OD at −80 °C. Figure 7 shows comparatively those of the complex solution prepared from Htppa and $[Cu^I(MeCN)_4]ClO_4$ in 1 : 1 molar ratio and its reaction solution with dioxygen at −80 °C, and the chemical shift values of the reaction solution in several temperatures are listed in Table 6 together with those of metal free Htppa. The formation of a 1 : 1 Cu(I)–Htppa system is clear from the

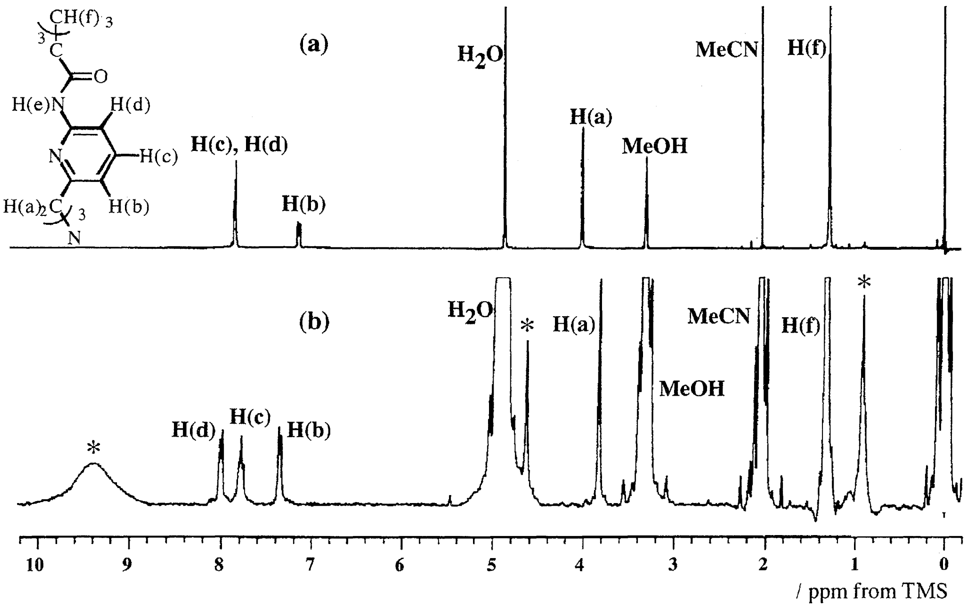

Fig. 7. ^{1}H NMR spectra for [Cu$^{\mathrm{I}}$(Htppa)]$^+$ and [Cu$^{\mathrm{II}}$(Htppa)(O_2^-)]$^+$ in CD_3OD at room temperature. *denote unknown peaks.

Table 6. ^{1}H NMR Chemical Shifts for Metal-Free Htppa, [Cu(Htppa)]$^+$, and [Cu(O_2^-)(Htppa)]$^+$ in CD_3OD

Sample	H(d)	H(c)	H(b)	H(e)	H(a)	H(f)
TPPA /+21 °C	7.96 (d, J=7.8, 1H)	7.74 (t, J=7.8, 1H)	7.32 (d, J=7.8, 1H)	—	3.78 (s, 2H)	1.31 (s, 9H)
Cu$^{\mathrm{I}}$–Htppa/+21 °C	7.85 (m, 2H)		7.15 (m, 1H)	—	4.01 (s, 2H)	1.28 (s, 9H)
Cu$^{\mathrm{II}}$–Htppa–O_2^-						
/−80 °C	8.00 (m, 1H)	7.82 (m, 1H)	7.53 (m, 1H)	—	3.71 (s, 2H)	1.28 (s, 9H)
−60 °C	7.98 (m, 1H)	7.79 (m, 1H)	7.40 (m, 1H)	—	3.74 (s, 2H)	1.30 (s, 9H)
−40 °C	7.98 (d, J=7.2, 1H)	7.79 (m, 1H)	7.38 (d, J=7.2, 1H)	—	3.76 (s, 2H)	1.30 (s, 9H)
−20 °C	7.97 (d, J=7.2, 1H)	7.75 (t, J=7.2, 1H)	7.34 (d, J=7.2, 1H)	—	3.79 (s, 2H)	1.31 (s, 9H)
0 °C	7.96 (d, J=7.2, 1H)	7.75 (t, J=7.2, 1H)	7.33 (d, J=7.2, 1H)	—	3.79 (s, 2H)	1.31 (s, 9H)
+21 °C	7.96 (d, J=7.2, 1H)	7.74 (t, J=7.2, 1H)	7.32 (d, J=7.2, 1H)	—	3.80 (s, 2H)	1.31 (s, 9H)

(in CD_3OD, δ ppm from TMS).

fact that the proton peaks of metal-free Htppa slightly shift to a lower-field region by the addition of [Cu$^{\mathrm{I}}$(MeCN)$_4$]ClO$_4$. Furthermore, their proton peaks slightly shifted to a lower-field region by the bubbling of dioxygen, whose spectra were typical of that of a diamagnetic species, although a few broad peaks of unknown origin were observed. The graduate increase of temperature of the reaction solution did not show remarkable line-broadenings and shifts due to the generation of paramagnetic species, suggesting that this Cu–O_2^- species is rather stable. However, the quick increasing gave paramagnetic spectra. The above-given results of the electronic absorption, ESR and NMR spectra all indicate that the reaction of [Cu(Htppa)]$^+$ complex with dioxygen generates [Cu(Htppa)(O_2^-)]$^+$ species which was antiferromagnetically coupled between the Cu(II) ion and O_2^-. The coordinated dioxygen seems to occupy the apical position in the trigonal-bipyramidal geometry of the copper complex from the electronic absorption spectra. The confirmation of the copper–dioxygen species was also attempted by resonance Raman spectral measurements with lasers of several wavelengths. However, all the samples irradiated showed immediate colour change with unsuccessful detection of the Cu–O_2^- bond, suggesting the photochemical decomposition of the complex.

The reversible binding of dioxygen upon copper ion center is of fundamental concern in chemical and biological processes. This copper–Htppa complex was also examined in several solutions. Interestingly, the bubbling of CO gas into a MeOH/THF/EtCN mixed solvent (4 : 3 : 3 volume ratio) of the superoxo species at −78 °C led to a significant color change, whose spectral change is presented in Fig. 8. The alternate bubblings of O_2 and CO into the solution exhibited a reversible change with an isosbestic point at 521 nm. The success of reversible uptake of O_2 in this mixed solvent may be understandable in terms of the solvent effect of redox potentials of the [CuCl(Htppa)]ClO$_4$ complex. This complex in a polar solvent such as MeOH gave lower redox potential values, whereas that in a non-polar solvent such as MeCN and CH_2Cl_2 indicated higher values; that in the intermediate solvent such as THF resulted in the intermediate value. The polar solvent causes a high valent copper to stabilize and the non-polar solvent causes a low valent copper to stabilize.

Recently, the Cu(II)-superoxide species synthesized by us was stated to be a mis-characterization of the Cu(II)–OH species.[30] However, we have independently reported that the reaction of [Cu(Htppa)]ClO$_4$ with dioxygen affords the [Cu-

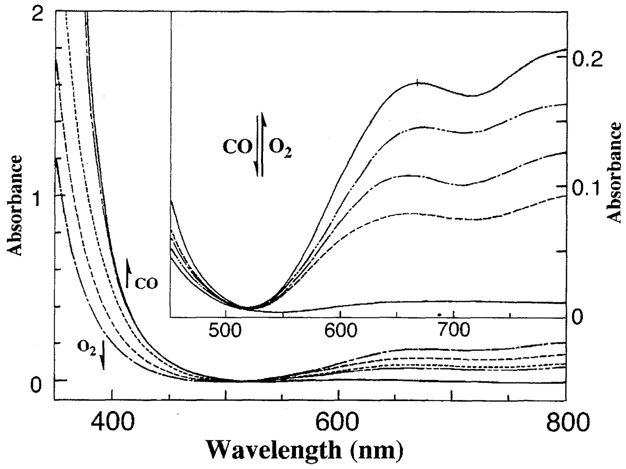

Fig. 8. Electronic absorption spectral change due to alternate bubbling of O_2 and CO into a MeOH/THF/EtCN mixed solution containing $[Cu(Htppa)]^+$ at −78 °C.

(OH)(Htppa)]ClO_4 complex, which has been characterized on the basis of X-ray and electronic absorption spectra.[36] Also, this hydroxo complex was obtained by quick increase of temperature of the solution containing $Cu(II)–O_2{}^-$ species up to r.t. and its absorption spectra was quite different from that of the $Cu(II)–O_2{}^-$ species. The most critical difference between them is their ^1H NMR spectra; that of [Cu(OH)-(Htppa)]ClO_4 was paramagnetic, although that obtained by the reaction of [Cu(Htppa)]ClO_4 with dioxygen was diamagnetic. The question raised by the recent note for this structure seems to have occured from our failure to present vibrational spectra for ν(O–O); regrettably our several attempts to record the spectra were unsuccessful, as was described above. Furthermore, the absorption spectra of the reaction solution containing $Cu(II)–O_2{}^-$ species, which was previously reported by us, had not been given in the commenting note. Our opinion is that the sample preparation procedure used by the scientists who submitted the note may be different from ours: The reaction solution obtained by simply mixing a methanol solution containing $[Cu(MeCN)_4]ClO_4$ with a methanol solution of Htppa at −78 °C is not quite sufficient to synthesize the $[Cu(Htppa)]^+$ complex with dioxygen, which sometimes happens in copper chemistry. Accordingly, all the results given here indicate that the $[Cu(Htppa)]^+$ complex reacts with the dioxygen to generate $[Cu(O_2{}^-)(Htppa)]^+$, whose characterization by a combination of electronic absorption, ESR and NMR spectra clearly support the formation of the $Cu(II)–O_2{}^-$ species.

We are grateful to Professor Osamu Yamauchi and Mr. Tatsuo Yajima, Nagoya University, for the use of the Varian VXR-300S NMR spectrometer, to the Institute for Molecular Science for the use of the JEOL Lambda-500 NMR spectrometer and Shimadzu KRATOS CONCEPT I S mass spectrometer. This research was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture. (M. H., K. J., and H. M.).

References

1) a) N. Kitajima, *Adv. Inorg. Chem.*, **39**, 1 (1992); b) K. D. Karlin, Z. Tyeklar, and A. D. Zuberbuhler, "Bioinorganic Catalysis," ed by J. Reedijk, Marcel Dekker, New York (1993), p. 261; c) Z. Tyeklar and K. D. Karlin, "Bionorganic Chemistry of Copper," ed by K. D. Karlin and Z. Tyeklar, Chapman & Hall, New York (1993), p. 277; d) J. P. Klinman, *Chem. Rev.*, **96**, 2541 (1996); e) E. I. Solomon, U. M. Sundaram, and T. E. Machonkin, *Chem. Rev.*, **96**, 2563 (1996).

2) a) I. Sanyal, P. Ghosh, and K. D. Karlin, *Inorg. Chem.*, **34**, 3050 (1995); b) K. D. Karlin, A. Nanthakumar, S. Fox, N. N. Murthy, N. Ravi, B. H. Huynh, R. D. Orosz, and E. P. Day, *J. Am. Chem. Soc.*, **116**, 4753 (1994); c) A. Nanthakumar, S. Fox, N. N. Murthy, and K. D. Karlin, *J. Am. Chem. Soc.*, **115**, 8513 (1993); d) F. Jiang, R. R. Conry, L. Bubacco, Z. Tyeklar, R. R. Jacobson, K. D. Karlin, and J. Peisach, *J. Am. Chem. Soc.*, **115**, 2093 (1993); e) K. Uozumi, Y. Hayashi, M. Suzuki, and A. Uehara, *Chem. Lett.*, **1993**, 963; f) A. Nanthakumar, M. S. Nasir, and K. D. Karlin, *J. Am. Chem. Soc.*, **114**, 6564 (1992); g) R. R. Jacobson, Z. Tyeklar, and K. D. Karlin, *Inorg. Chim. Acta*, **181**, 111 (1991); h) H. Baek, K. D. Karlin, and R. A. Holwerda, *Inorg. Chem.*, **25**, 2347 (1986); i) G. Kokoszka, K. D. Karlin, F. Padula, J. Baranowski, and C. Goldstein, *Inorg. Chem.*, **23**, 4378 (1984); j) H. K. Baek and R. A. Holwerda, *Inorg. Chem.*, **22**, 3452 (1983); k) C. Chuang, K. Lim, Q. Chen, and J. W. Zubieta, *Inorg. Chem.*, **34**, 2562 (1995).

3) M. R. Malachowski, H. B. Huynh, L. J. Tomlinson, R. S. Kelly, and J. W. J. Furbee, *J. Chem. Soc., Dalton Trans.*, **1995**, 31.

4) R. Uma, R. Viswanathan, M. Palaniandavar, and M. Laksminarayanan, *J. Chem. Soc., Dalton Trans.*, **1994**, 1219.

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

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

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

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

9) R. R. Jacobson, Z. Tyeklar, K. D. Karlin, and J. Zubieta, *Inorg. Chem.*, **30**, 35 (1991).

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

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

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

13) K. D. Karlin, J. C. Hayes, S. Juen, J. P. Hutchinson, and J. Zubieta, *Inorg. Chem.*, **21**, 4106 (1982).

14) K. D. Karlin, J. C. Hayes, J. P. Hutchinson, J. R. Hyde, and J. Zubieta, *Inorg. Chim. Acta*, **64**, L219 (1982).

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

16) M. Harata, K. Jitsukawa, H. Masuda, and H. Einaga, *J. Coord. Chem.*, in press (1997).

17) A. Wada, M. Harata, K. Hasegawa, K. Jitsukawa, H. Masuda, M. Mukai, T. Kitagawa, and H. Einaga, *Angew. Chem.*, in press (1998).

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

19) N. Kitajima, K. Fujisawa, C. Fujimoto, Y. Moro-oka, S. Hashimoto, T. Kitagawa, K. Toriumi, K. Tatsumi, and A. Nakamura, *J. Am. Chem. Soc.*, **114**, 1277 (1992).

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

21) a) D. E. Wilcox, J. R. Long, and E. I. Solomon, *J. Am. Chem. Soc.*, **106**, 2186 (1984); b) G. L. Woolery, L. Powers, M. Winkler, E. I. Solomon, and T. G. Spiro, *J. Am. Chem. Soc.*, **106**, 86 (1984); c) R. S. Himmelwright, N. C. Eickman, C. D. LuBien, and E. I. Solomon, *J. Am. Chem. Soc.*, **102**, 5378 (1980); d) R. S. Himmelwright, N. C. Eickman, and E. I. Solomon, *J. Am. Chem. Soc.*, **101**, 1576 (1979).

22) a) E. I. Solomon, in "Metal Clusters in Proteins," ed by L. Que, Jr., ACS Symposium Series No. 372, American Chemical Society, Washington, D.C. (1988), p. 116; b) E. I. Solomon, K. W. Penfield, and D. E. Wilcox, *Struct. Bond.*, **53**, 1 (1983).

23) R. S. Himmelwright, N. C. Eickman, C. D. LuBien, K. Lerch, and E. I. Solomon, *J. Am. Chem. Soc.*, **102**, 7339 (1980).

24) a) M. J. Ettinger and D. J. Kosman, in "Copper Proteins," ed by T. G. Spiro, Wiley, New York (1981), p. 219; b) B. J. Marwedel, D. J. Kosman, R. D. Bereman, and R. J. Kurland, *J. Am. Chem. Soc.*, **103**, 2842 (1981).

25) a) D. M. Dooley and M. A. McGuirl, *Inorg. Chim. Acta*, **123**, 231 (1986); b) D. M. Dooley and C. E. Cote, *Inorg. Chem.*, **24**, 3996 (1985); c) D. M. Dooley and K. C. Golnik, *J. Biol. Chem.*, **258**, 4245 (1983); d) K. D. S. Yadav and P. F. Knowles, *Eur. J. Biochem.*, **114**, 139 (1981); e) I. D. Kelly, P. F. Knowles, K. D. S. Yadav, W. G. Bardsley, P. Leff, and R. D. Waight, *Eur. J. Biochem.*, **114**, 133 (1981); f) R. Barker, N. Boden, G. Cayley, S. C. Charlton, R. Henson, M. C. Holmes, I. D. Kelly, and P. F. Knowles, *Biochem. J.*, **177**, 289 (1979).

26) a) L. Casella, M. Gullotti, A. Pintar, G. Pallanza, and A. Marchesini, *J. Inorg. Biochem.*, **37**, 105 (1989); b) L. Casella, M. Gullotti, G. Pallanza, A. Pintar, and A. Marchesini, *Biochem. J.*, **251**, 441 (1988); c) T. Sakurai, S. Sawada, S. Suzuki, and A. Nakahara, *Biochim. Biophys. Acta*, **915**, 238 (1987).

27) a) D. M. Dooley and M. A. McGuirl, *Inorg. Chem.*, **26**, 1261 (1986); b) I. Bertini, G. Lanini, C. Luchinat, L. Messori, R. Monnanni, and A. Scozzafava, *J. Am. Chem. Soc.*, **107**, 4391 (1985); c) K. G. Strothkamp and S. J. Lippard, *Biochemistry*, **20**, 7488 (1981).

28) M. Harata, K. Jitsukawa, H. Masuda, and H. Einaga, *J. Am. Chem. Soc.*, **116**, 10817 (1994).

29) M. Harata, K. Jitsukawa, H. Masuda, and H. Einaga, *Chem. Lett.*, **1995**, 61.

30) L. M. Berreau, S. Mahapatra, J. A. Halfen, V. G. Young, Jr., and W. B. Tolman, *Inorg. Chem.*, **35**, 6339 (1996).

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

32) Enraf–Nonius, "MolEN, An Interactive Structure Solution Procedure," Enraf–Nonius, Delft, The Netherlands (1990).

33) B. J. Hathaway, in "Comprehensive Coordination Chemistry," ed by TS. G. Wilkinson, Pergamon Press, Oxford (1987), p. 533.

34) J. O'M. Bockris and A. K. N. Reddy, "Modern Electrochemistry," Plenum Press, New York (1970).

35) a) K. D. Karlin, N. Wei, B. Jung, S. Kaderli, P. Niklaus, and A. D. Zuberbuhler, *J. Am. Chem. Soc.*, **115**, 9506 (1993); b) N. Wei, N. N. Murthy, Z. Tyklar, and K. D. Karlin, *Inorg. Chem.*, **33**, 1177 (1994); c) N. Wei, N. N. Murthy, Q. Chen, J. Zubieta, and K. D. Karlin, *Inorg. Chem.*, **33**, 1953 (1994).

36) M. Harata, K. Jitsukawa, H. Masuda, and H. Einaga, *Chem. Lett.*, **1996**, 813.