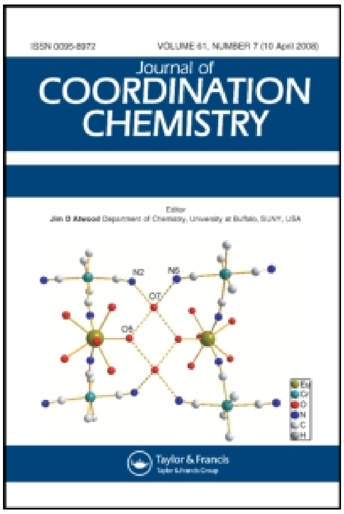

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PREPARATION, STRUCTURE AND PROPERTIES OF A COPPER(II) COMPLEX WITH A NEW TRIPODAL TETRADENTATE LIGAND, *BIS*{(6-PIVALOYLAMINO-2-PYRIDYL)METHYL}{(5-CARBOXY-2-PYRIDYL)METHYL}AMINE (BPCA), AND REACTION OF ITS Cu(I) COMPLEX WITH DIOXYGEN

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PREPARATION, STRUCTURE AND PROPERTIES OF A COPPER(II) COMPLEX WITH A NEW TRIPODAL TETRADENTATE LIGAND, *BIS*{(6-PIVALOYLAMINO-2-PYRIDYL)METHYL}{(5-CARBOXY-2-PYRIDYL)METHYL}AMINE (BPCA), AND REACTION OF ITS Cu(I) COMPLEX WITH DIOXYGEN

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A copper complex with a new tripodal tetradentate ligand, *bis*{(6-pivaloylamino-2-pyridyl)-methyl}{(5-carboxyl-2-pyridyl)methyl}amine (BPCA), has been prepared as a model metal centre of copper enzymes that react with dioxygen, the behaviour of which in solution has been examined on the basis of absorption and ESR spectra. Addition of NaN_3 to an H_2O/CH_3OH solution containing $Cu(ClO_4)_2 \cdot 6H_2O$–BPCA with 1 : 1 molar ratio has afforded the complex [Cu-(bpca)(N_3)]ClO_4. It crystallizes in the monoclinic space group $P2/a$, $a = 17.478(3)$, $b = 9.773(1)$, $c = 22.388(5)$ Å, $\beta = 102.92(2)°$, $Z = 4$. The crystal structure reveals that the coordination around the central metal ion forms a trigonal bipyramid with three pyridine nitrogen atoms of BPCA (Cu–N(2) = 2.01(2), Cu–N(3) = 2.09(1) and Cu–N(4) = 2.22(1) Å) in the trigonal plane and with a tertiary amino nitrogen atom of BPCA (Cu–N(1) = 1.99(1) Å) and an azide anion (Cu–N(7) = 1.96(2) Å) in axial positions. The azide ion is coordinated in an end-on configuration, the coordinating nitrogen of which forms hydrogen bonds with two amide NH groups of BPCA; the terminal nitrogen is weakly bound with the carboxyl group of BPCA by hydrogen bonds through a water molecule. Cyclic voltammetry of an acetonitrile solution containing $Cu(ClO_4)_2 \cdot 6H_2O$–BPCA–KCl with 1 : 1 : 1 molar ratio exhibits reversible one-electron redox behaviour with $E_{1/2} = +0.24$ V *vs* NHE, indicating that the BPCA ligand can stabilize the lower oxidation state of copper. Reaction of [Cu^I(bpca)]ClO_4 with dioxygen in methanol or propionitrile at −78°C gives marked absorption changes which suggest the formation of a Cu–O_2 complex.

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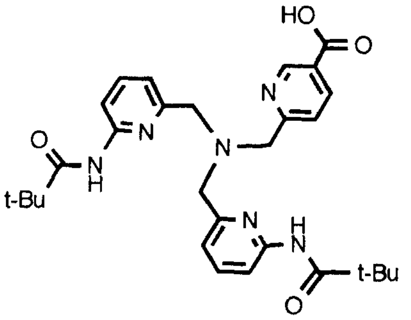
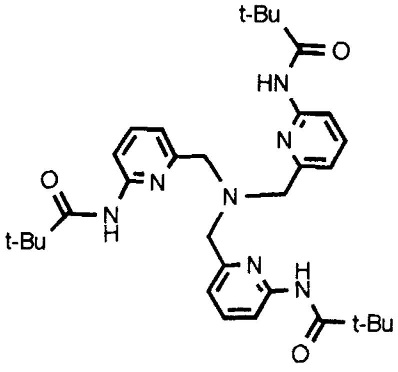
Keywords: Tripodal tetradentate ligand; copper-oxygen adduct; crystal structure; copper complex

INTRODUCTION

Tripodal ligands are frequently used in bioinorganic studies as they form coordination structures similar to the active site in metal enzymes and allow tuning of steric and electronic properties of the metal centre. Many copper complexes with such low-molecular weight ligands, which contain pyridine,[1-15] quinoline,[5,7] imidazole,[8-13] pyrazole,[11,12,15-17] and imidazolyl donor groups,[18] have been prepared as structural and/or functional models for copper-containing enzymes such as hemocyanin,[19,20] tyrosinase,[21] galactose oxidase,[22] amine oxidase,[23] ascorbate oxidase,[24] and superoxide dismutase.[25] Most interest has been focussed on the binding and activation of dioxygen. We have previously succeeded in causing uptake of dioxygen as a superoxide on a mononuclear copper complex with a tripodal tetradentate ligand, *tris*{(6-pivaloylamino-2-pyridyl)methyl}amine (TPPA) (below),[26,27] in which the coordination of the superoxide is stabilized by hydrogen bonds with the amide NH groups of the TPPA ligand. In order to enhance reactivity with dioxygen, we have synthesized another new tripodal ligand, *bis*{(6-pivaloylamino-2-pyridyl)methyl}{(5-carboxyl-2-pyridyl)methyl)amine (BPCA) and its copper(II) complexes, which have the ability to react with a substrate.



bpca



tppa

Here, we describe the synthesis of the Cu-BPCA complex and the structural and electrochemical characterization of the species generated by reaction with an azide anion. The N_3^- is probably the most widely used ligand probe for copper protein sites and is often employed as a structural model for metal-oxygen coordination.[19] [25]

EXPERIMENTAL

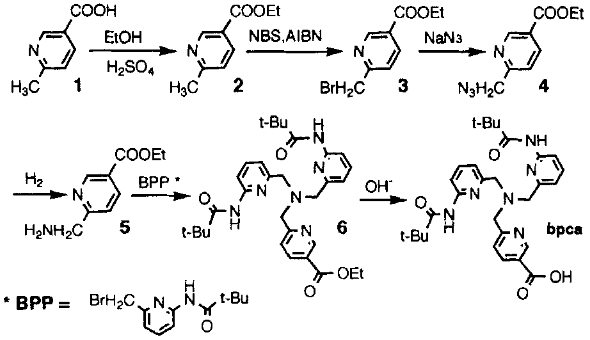
Materials and Measurements

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

Electronic absorption spectra were recorded at −78°C on a Jasco UVI-DEC-660 spectrophotometer equipped with a low temperature cell. X-band ESR spectra of frozen solutions were recorded at 77 K using a Jeol RE-1X ESR spectrometer. The samples for both measurements were prepared in methanol (MeOH), acetonitrile (MeCN) or propionitrile (EtCN). ^{1}H NMR spectra were measured in $CDCl_3$ or DMSO-d_6 with TMS as internal standard on a Varian VXR-300S or Jeol Lambda-500 spectrometer. Positive-ion FAB mass spectra were obtained with a Shimadzu Kratos CONCEPT I S mass spectrometer. Cyclic voltammetric measurments were performed using a Bioanalytical Systems (BAS) CV-27 instrument equipped with a Graphtec X–Y WX2400 chart recorder. A 3 mm diameter glassy-carbon working electrode, an Ag/Ag$^+$ reference electrode, and a Pt wire counter electrode were used in a glass cell having a working compartment with approximately 3 cm^3 in volume. All measurements were made at 25°C under an argon atmosphere in MeCN with tetra(*n*-butyl)ammonium tetrafluoroborate (0.1 M, 1 M = 1 mol dm^{-3}) as supporting electrolyte at a scan rate of 100 mV/s. Electrochemical potentials are reported *vs* the normal hydrogen electrode (NHE) by addition of 490 mV.

Syntheses of BPCA

BPCA was prepared from 6-methylnicotinic acid (**1**) according to the following procedure (Scheme 1).



SCHEME 1.

6-Methylnicotinic Acid Ethyl Ester (**2**)

Esterification of **1** was carried out according to the procedure of ref. 28. An EtOH solution of **1** (0.55 g, 4.0 mmol) was refluxed for 8 h in the presence of a catalytic amount of H_2SO_4. After evaporation of EtOH, the residue was extracted with chloroform and then dried over $MgSO_4$. The solvent was removed *in vacuo* to give 0.66 g (100% yield) of a light-yellowish oil, **2**: ^{1}H NMR ($CDCl_3$) δ 1.70 (t, 3H, CH_2CH_3), 2.63 (s, 3H, pyridine 6-CH_3), 4.28 (q, 2H, CH_2CH_3), 7.19 (d, 1H, pyridine 5-H), 8.18 (d, 1H, pyridine 4-H), 9.13 (s, 1H, pyridine 2-H).

6-Bromomethylnicotinic Acid Ethyl Ester (**3**)

To a 50 cm^3 CCl_4 solution of **2** (0.66 g, 4.0 mmol) under a nitrogen atmosphere was added NBS (0.71 g, 4.0 mmol) and a catalytic amount of AIBN. The resulting mixture was refluxed for 2 h. After cooling, the solution containing the monobromide **3**, dibromide as a by-product, and unreacted **2** was washed with a 5% sodium bicarbonate solution and then dried over $MgSO_4$. After evaporation, purification by column chromatography on silica gel with hexane-AcOEt (5 : 1) as eluent gave 0.41 g of **3** (42% yield). ^{1}H NMR ($CDCl_3$) δ 1.41 (t, 3H, CH_2CH_3), 4.40 (q, 2H, CH_2CH_3), 4.58 (s, 2H, CH_2Br), 7.55 (d, 1H, pyridine 5-H), 8.30 (d, 1H, pyridine 4-H), 9.17 (s, 1H, pyridine 2-H).

6-Azidomethylnicotinic Acid Ethyl Ester (**4**)

A DMF solution (50 cm^3) containing NaN_3 (0.30 g, 3.1 mmol) and **3** (0.66 g, 2.7 mmol) was stirred for 2 h at 100°C. After cooling, H_2O (50 cm^3) was added to the solution. The mixture was extracted with ether, washed with H_2O and brine, and then dried over $MgSO_4$. Removal of the solvent *in vacuo* gave 0.53 g of **4** (95% yield). ^{1}H NMR (DMSO-d_6) δ 1.40 (t, 3H, CH_2CH_3), 4.42 (q, 2H, CH_2CH_3), 4.58 (s, 2H, CH_2N_3), 7.41 (d, 1H, pyridine 5-H), 8.35 (d, 1H, pyridine 4-H), 9.19 (s, 1H, pyridine 2-H).

6-Aminomethylnicotinic Acid Ethyl Ester (**5**)

A 50 cm^3 MeOH solution of **4** (0.53 g, 2.6 mmol) and 0.2 g of 10% palladium on carbon catalyst were placed under a hydrogen atmosphere (3 atm) and stirred for 3 h. After removal of the catalyst and solvent, 0.46 g of **5** was quantitatively obtained as a yellow powder (100% yield). ^{1}H NMR ($CDCl_3$) δ 1.41 (t, 3H, CH_2CH_3), 1.97 (s, 2H, NH_2), 4.38 (q, 2H, CH_2CH_3), 4.47 (s, 2H, CH_2NH_2), 7.79 (d, 1H, pyridine 5-H), 8.41 (d, 1H, pyridine 4-H), 9.17 (s, 1H, pyridine 2-H).

BPCA Ethyl Ester (6)

Coupling of the primary amine **5** (0.46 g, 2.6 mmol) with the two equivalent of 2-bromomethyl-6-pivaloylaminopyridine (1.80 g, 6.5 mmol) was carried out in a 50 cm^3 dioxane solution in the presence of $NaHCO_3$ (2.10 g, 2.5 mmol) in H_2O (50 cm^3). The reaction mixture was stirred for 2 days and then neutralized with 1M HCl. After evaporation of the solvent, the residue was extracted with $CHCl_3$ and dried over $MgSO_4$. The solvent was removed *in vacuo* to give a crude brown oil, which was purified by column chromatography on silica gel with hexane–AcOEt–MeOH (20 : 5 : 1) as eluent. Removal of the solvent gave 0.48 g of **6** (33% yield). ^{1}H NMR ($CDCl_3$) δ 1.37 (s, 18H, tert-Bu), 1.40 (t, 3H, CH_2CH_3), 3.78 (s, 4H, NCH_2), 3.95 (s, 2H, NCH_2), 4.42 (q, 2H, CH_2CH_3), 7.21 (d, 2H, pyridine-H), 7.63 (d, 1H, pyridine-H), 7.69 (t, 2H, pyridine-H), 8.15 (d, 2H, pyridine-H), 8.27 (d, 1H, pyridine-H), 8.38 (s, 2H, amido-NH), 9.10 (s, 1H, pyridine 2-H).

BPCA (7)

A suspension of **6** (0.48 g, 0.86 mmol) in dioxane/H_2O (50 cm^3/50 cm^3) containing KOH (0.18 g, 3.2 mmol) was stirred for 0.5 h at room temperature, neutralized with 1 M HCl and evaporated *in vacuo*. The residue was desalted with EtOH to give BCPA **7** (0.45 g, 98% yield) as a brownish oil. ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 18H, tert-Bu), 3.77 (s, 4H, NCH_2), 3.94 (s, 2H, NCH_2), 7.26 (d, 2H, pyridine-H), 7.66 (d, 1H, pyridine-H), 7.67 (t, 2H, pyridine-H), 8.07 (s, 2H, amido-NH), 8.11 (d, 2H, pyridine-H), 8.25 (d, 1H, pyridine-H), 9.12 (s, 1H, pyridine 2-H). Positive ion FAB-mass spectra: m/z = 533 $[M+H]^+$ and 555 $[M+Na]^+$.

Reaction of [Cu(bpca)]PF_6 with Dioxygen

To a EtCN solution (5 cm^3, 3mM) of $[Cu(MeCN)_4](PF_6)$ (5.6 mg, 0.32 mmol) thoroughly degassed with Ar was added BPCA (8.0 mg, 0.32 mmol); this solution was used for the reaction with dioxygen. The preparation of a MeOH solution was performed by the same method with MeOH (5 cm^3, 1 mM), $[Cu(MeCN)_4](PF_6)$ (1.9 mg, 0.10 mmol) and BPCA (2.7 mg, 0.10 mmol).

Preparation of Crystalline [Cu(bpca)(N_3)]ClO_4 (8)

To a stirred aqueous MeOH solution (5 cm^3, 10 : 1) of $Cu(ClO_4)_2 \cdot 6H_2O$ (3.7 mg, 0.01 mmol) and BPCA (5.3 mg, 0.21 mmol) was added NaN_3 (0.8 mg, 0.012 mmol). The mixture was allowed to stand for several days at room temperature when green plate-like single crystals of [Cu(bpca)(N_3)]-ClO_4 (**8**) suitable for X-ray crystal structure analysis were obtained.

X-ray Structure Analysis of [Cu(bpca)(N_3)]$ClO_4 \cdot 4.5H_2O$ (8)

The crystal was mounted on a glass capillary. Diffraction data were collected with graphite-monochromated MoKα radiation on an Enraf-Nonius CAD4-EXPRESS four circle diffractometer at room temperature with the $\omega-2\theta$ scan technique. Crystal data and experimental details are listed in Table I.

The structure was solved by a combination of direct methods and Fourier techniques, and was anisotropically refined for non-hydrogen atoms by full-matrix least-squares calculations. Refinement was 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.[29] Empirical absorption corrections using DIFABS[30] were applied 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 for the most part. All calculations were

TABLE I Crystallographic data for [Cu(bpca)(N_3)]$ClO_4 \cdot 4.5H_2O$

Formula	$C_{29}H_{45}N_9O_{12.5}CuCl$
F.W.	818.73
Colour	Green
Crystal dimensions/mm	0.1 × 0.3 × 0.4
Crystal system	Monoclinic
Space group	$P2/a$
a/Å	17.478(3)
b/Å	9.773(1)
c/Å	22.388(5)
β/deg	102.92(2)
V/Å^3	3727(1)
D_{calc}/g cm^{-3}	1.460
Z	4
F(000)	1712.0
μ (MoKα)/cm^{-1}	7.30
Radiation	Graphite monochromated MoKα ($\lambda = 0.71073$ Å)
T/°C	21
$2\theta max$/deg	48.6
No. of reflections measured/total; unique	6608; 6438 ($R_{int} = 0.078$)
No. of reflections used [$I > 2.00\sigma(I)$]	2067
R; R_w[a]	0.107; 0.069

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

carried out on an SGI IRIS Indigo XS-24 workstation using the teXsan program.[31]

RESULTS AND DISCUSSION

Absorption and ESR Spectra of Cu(II)–BPCA Systems

The absorption spectra of Cu(II)–BPCA systems showed different d-d bands in the range 600–1000 nm depending on counter anions (Table II). The [Cu(bpca)](ClO_4)$_2$ complex gave d-d bands at 595 and 721 nm in MeOH and MeCN solutions, respectively, both of which are typical of a square planar Cu(II) complex.[32] The spectra obtained by addition of NaCl to a MeOH or MeCN solution of [Cu(bpca)](ClO_4)$_2$ (725, 844 nm in MeOH and 725, 855 nm in MeCN, respectively) and those by addition of NaN_3 to a MeOH or MeCN solution (654, 841 nm in MeOH and 660, 836 nm in MeCN, respectively) suggested that their Cu(II) complexes have a trigonal bipyramidal structure, the latter of which showed charge transfer (CT) bands at 388 and 389 nm in MeOH and MeCN, respectively. The Cu(II)–BPCA–OH system in MeOH (608, 800(sh) nm) and MeCN (598, 800(sh) nm) solutions gave the patterns typical of a square pyramidal geometry.

ESR measurements of MeOH solutions of these Cu(II)–BPCA systems at 77 K gave spectra characteristic of a $d_{x^2-y^2}$ ground state of a Cu(II) complex,[32] although they were complicated due to the existence of several species. This supports the structures suggested by the absorption spectra. Unfortunately, MeCN solutions did not give any well-defined spectra.

Crystal Structure of [Cu(bpca)(N_3)]ClO_4 (8)

The slow evaporation of a CH_3OH/H_2O solution containing [Cu(bpca)]-(ClO_4)$_2$ and NaN_3 in the molar ratio 1 : 1 at room temperature gave single crystals of [Cu(bpca)(N_3)]ClO_4 (**8**) suitable for X-ray structural analysis.

TABLE II Electronic spectroscopy data for the Cu(II)–BPCA–Anion systems

Anion	λmax, (ε)/nm, ($M^{-1}\,cm^{-1}$)	
	MeCN	*MeOH*
(ClO_4^-)	721(186)	595(165)
Cl^-	855(227), 725(179)	844([a]), 725([a])
N_3^-	836(232), 660(229), 389(2120)	841(197), 654(206), 388(985)
OH^-	800(90, sh), 598(157)	800([a], sh), 608([a])

[a] The ε value is unknown for partial precipitation.

The complex crystallizes in the monoclinic space group *P*2/*a* with four discrete $[Cu(bpca)(N_3)]^+$ cations and four perchlorate anions in the unit cell. Selected bondlengths and angles are listed in Table III and an ORTEP drawing of the $[Cu(bpca)(N_3)]^+$ cation is depicted in Figure 1.

As suggested above, the structure of complex **8** in the crystal has an axially-compressed trigonal bipyramidal geometry with three pyridyl nitrogens

TABLE III Selected bondlengths (Å) and angles (deg) for $[Cu(bpca)(N_3)]ClO_4 \cdot 4.5H_2O$

Cu(1)-N(1)	1.99(1)	Cu(1)-N(4)	2.22(1)
Cu(1)-N(2)	2.01(2)	Cu(1)-N(7)	1.96(2)
Cu(1)-N(3)	2.09(1)		
N(1)-Cu(1)-N(2)	82.7(8)	N(2)-Cu(1)-N(4)	120.0(7)
N(1)-Cu(1)-N(3)	81.5(6)	N(2)-Cu(1)-N(7)	100.6(8)
N(1)-Cu(1)-N(4)	80.6(7)	N(3)-Cu(1)-N(4)	106.6(5)
N(1)-Cu(1)-N(7)	176.4(7)	N(3)-Cu(1)-N(7)	95.3(6)
N(2)-Cu(1)-N(3)	127.1(7)	N(4)-Cu(1)-N(7)	98.9(7)

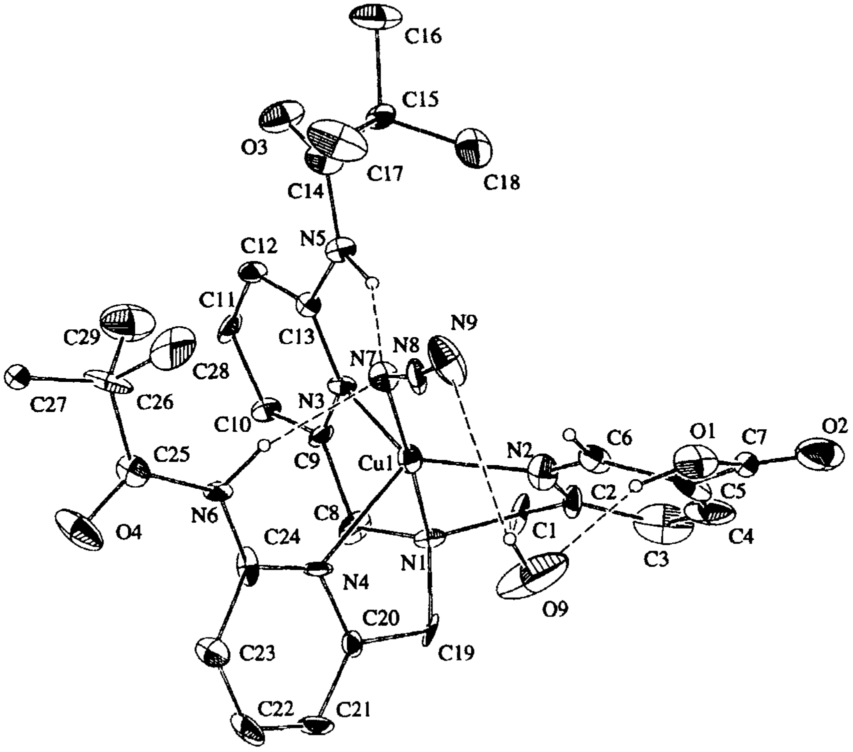


FIGURE 1 Molecular structure of $[Cu(bpca)(N_3)]^+ \cdot (H_2O)$, with the atom numbering scheme, showing the hydrogen bond networks.

of BPCA in the trigonal plane (Cu–N(2) = 2.01(2) Å, Cu–N(3) = 2.09(1) Å, Cu–N(4) = 2.22(1) Å) and with a tertiary amino nitrogen (Cu–N(1) = 1.99(1) Å) in the axial position. The remaining axial position is occupied by an azide anion in an end-on configuration (Cu–N(7) = 1.96(2) Å, Cu–N(7)–N(8) = 128(1)°). The coordination geometry around the Cu(II) ion is very similar to the geometries of Cu(II) complexes containing the TPPA ligand, [Cu(tppa)Cl]ClO_4,[27] [Cu(tppa)(OH)]ClO_4,[33] and [Cu(tppa)(O_2)]-ClO_4,[26] reported previously. The almost linear N–N–N bond vector (N(7)–N(8)–N(9) = 170(2)°) is directed to the carboxylate oxygen substituted at the 5-position of one pyridine ring of BPCA, in which the pyridine ring and carboxylate plane are slightly twisted with a 21(3)° dihedral angle for C(6)–C(5)–C(7)–O(1). The azide anion and the carboxyl oxygen are weakly bound through a water molecule, although the distances, N(9)···O(9) = 3.50 Å and O(1)···O(9) = 2.99 Å, are somewhat long for a hydrogen bond. Furthermore, two N–H bond vectors of BPCA are directed to the azide anion (N(5)···N(7) = 2.86 Å N(6)···N(7) = 3.05 Å), suggesting that coordination of azide is stabilized through hydrogen bonds.

Cyclic Voltammetry

Cyclic voltammograms of the complexes [Cu(bpca)Cl]ClO_4 and [Cu(bpca)-(N_3)]ClO_4 in MeCN under argon showed almost reversible one-electron redox behaviour with a pair of cathodic and anodic waves for Cu(II)/Cu(I), the parameters of which are given in Table IV. $E_{1/2}$ values of these complexes are −0.249 and −0.400 V *vs* Ag/Ag^+ (+0.241 and +0.090 V when converted to the NHE scale by the addition of +0.490 V), respectively, significantly higher than the $E_{1/2}$ value of the complex [Cu(tmpa)Cl]PF_6 (tmpa = *tris*{(2-pyridyl)methyl}amine) (−0.39 V *vs* NHE),[34] but lower than that of [Cu(tppa)Cl]ClO_4 (+0.447 V *vs* NHE).[27] The order of these redox potentials, *i.e.*, tmpa < bpca < tppa complexes, may be explained in terms of

TABLE IV Cyclic voltammetry data for several Cu(II)/complexes at room temperature

Complex	$E_{1/2}{}^a$/V	ΔEp/V	i_{pa}/i_{pc}	*Reference*
[Cu(tmpa)(Cl)]PF_6	−0.39		0.95	[b]
[Cu(bpca)(Cl)]ClO_4	+0.241(−0.249 *vs* Ag/Ag^+)	0.067	0.92	This work
[Cu(bpca)(N_3)]ClO_4	+0.090(−0.400 *vs* Ag/Ag^+)	0.120	1.00	This work
[Cu(tppa)(Cl)]ClO_4	+0.447(+0.225 *vs* Ag/AgCl)	0.090	0.95	[c]

[a] $E_{1/2} = (E_{pa} + E_{pc})/2$; The values are converted to the NHE scale by addition of 490 and 225 mV for Ag/Ag^+ and Ag/AgCl scales, respectively.

[b] Values from Ref. 32.

[c] Values from Ref. 27.

electron densities on the central metal ion. The electron-withdrawing pivalamide group decreases electron density and thus increase the redox potential. The TPPA ligand, which is substituted with three pivalamide groups, stabilizes the lower oxidation state of copper in comparison with the other two ligands. Substitution of carboxyl group at the *meta* position of pyridine may not contribute to the redox potential, although it is also electron-withdrawing in nature.

Reaction of [Cu^I(bpca)]PF$_6$ with Dioxygen

Bubbling of dioxygen to an EtCN solution containing [Cu^I(bpca)]PF$_6$ at −78°C caused a drastic absorption change as shown in Figure 2(a). The two d-d bands in range 600–1000 nm increased with time; they give a spectroscopic pattern typical of a Cu(II) complex with a trigonal bipyramidal geometry. In addition, two absorption bands at 370 ($\varepsilon = 450\,M^{-1}cm^{-1}$) and 507 nm ($\varepsilon = \sim 100\,M^{-1}cm^{-1}$) rapidly increased simultaneously with reaction with dioxygen; the former band is assignable to LMCT due to the formation of the Cu–O$_2$ complex by comparison with those reported previously.[26] The smaller LMCT band in comparison with the usual one may be due to distorted Cu–O$_2$ coordination caused by bulky substituent groups. These bands disappeared after 5 h, and completely at high temperature. Similar spectroscopic changes were also detected in a MeOH solution (Figure 2(b)), although there are some differences in detail. The two d-d bands, which suggest trigonal bipyramidal geometry, appear in the range 600–900 nm. Two intense bands were also observed at 380 ($\varepsilon = 680\,M^{-1}$ cm^{-1}) and 617 nm ($\varepsilon = 221\,M^{-1}cm^{-1}$), although they shift to longer wavelength in comparison with those in EtCN; these bands also disappeared at high temperature. The change in MeOH is more rapid than that in EtCN. In both MeOH and EtCN solutions, the spectra of the d-d region with increasing temperature are almost the same as those measured immediately after the reaction of the Cu(I) species with dioxygen, indicating that the coordination geometries around copper are almost the same.

The reaction of [Cu^I(bpca)]PF$_6$ with dioxygen was also followed by ESR measurements. These gave weak signals due to the Cu(II) species, although completely ESR silent spectra suggesting the formation of the Cu(II)–O$_2^-$ complex were expected. This complex may be quite sensitive to air. As deduced from the absorption spectra, the reaction of those complexes with dioxygen is very fast in comparison with that of [Cu^I(tppa)]ClO$_4$. Judging from structural aspects, the Cu atom in the BPCA complex is highly exposed to solvent in comparison with that in the TPPA complex. ESR

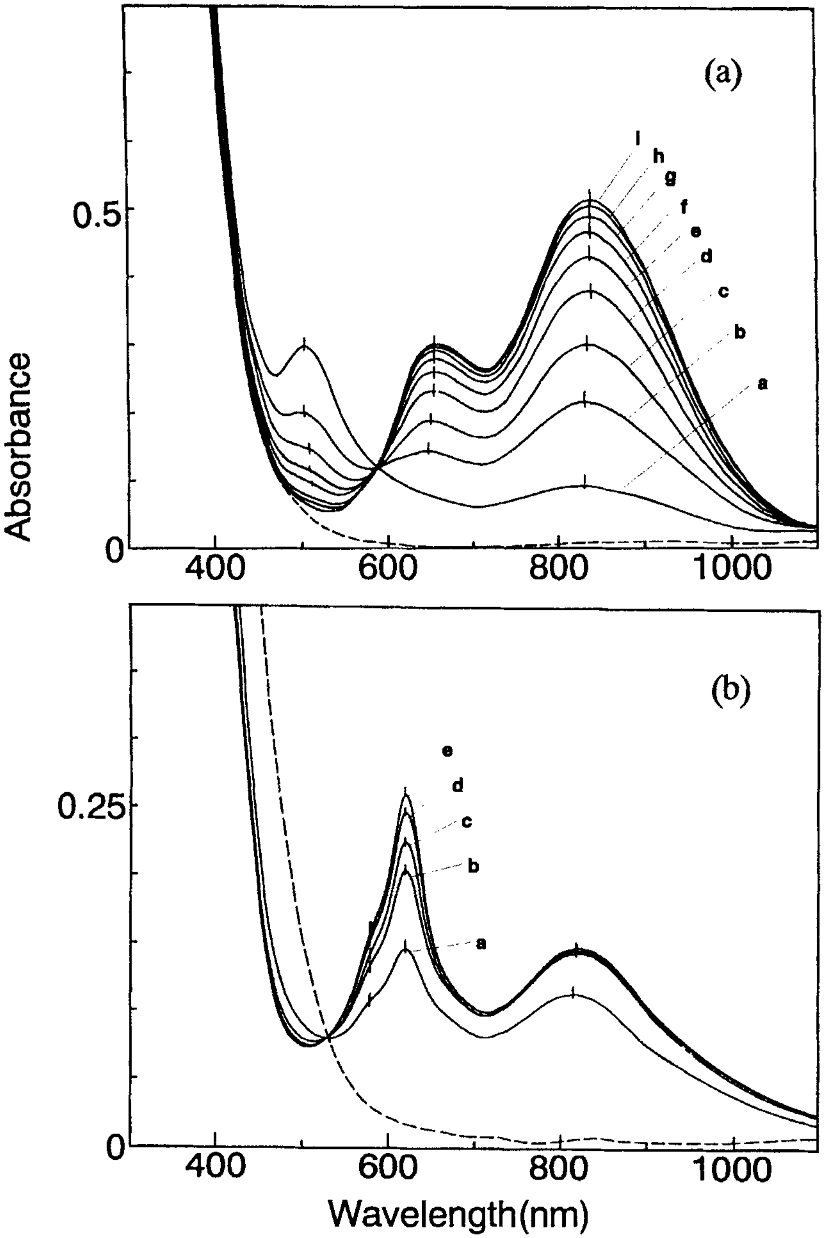


FIGURE 2 Absorption spectroscopic change for the reaction of [Cu(bpca)]PF_6 with dioxygen in EtCN (a) and MeOH (b) at −78°C. The course of the reaction with dioxygen is as follows: (---) [Cu(bpca)]PF_6, (——) time course in the reaction {[Cu(bpca)]PF_6 + O_2} ((a) → a → b → c → d → e → f → g → h → i (time interval, 30 min); (b) → a → b → c → d → e (time interval, 10 min)).

spectra measured after reaction suggested a typical trigonal bipyramidal Cu(II) complex. The electronic absorption and ESR spectroscopy behaviour and the comparison of the results reported previously suggest the formation of the Cu(II)–O_2^- species.[26]

In order to construct a model metal centre for copper oxygenase in biological systems, we have undertaken the design and preparation of Cu-BPCA. The BPCA complex exhibits a high redox potential, which stabilizes the Cu(I) complex that enables binding of a dioxygen molecule. The formation of $[Cu(bpca)(N_3)]^+$ as a structural model of the Cu(II)–O_2^- complex was confirmed crystallographically. Reaction of $[Cu^I(bpca)]PF_6$ with dioxygen in a MeOH or EtCN solution showed a typical spectroscopic pattern suggesting the formation of Cu(II) species and CT from superoxide to Cu(II). The present results suggest that the coordination environment and electronic state of the copper atom in biological systems may be similar to those formed in our TPPA and BPCA complexes.

SUPPLEMENTARY MATERIAL

A full list of atomic coordinates, thermal parameters and torsion angles for non-H atoms and tables of calculated and observed structure factors is available from the authors on request.

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