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Copper(I) Complexes with Pyridyl- and Imidazoyl-Containing Tripodal Tetradentate Ligands and Their Reactions with Dioxygen

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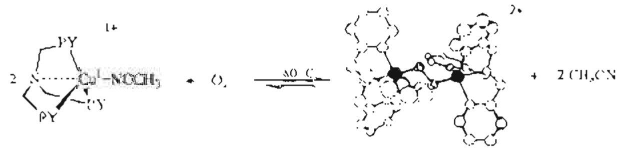
Continuing investigations of copper(I) complex reactions with dioxygen have led us to utilize imidazoyl-containing ligands, with the potential to reveal more about these donor ligand groups of significance in copper-containing proteins. The tripodal tetradentate ligands BPIA (bis((2-pyridyl)methyl)((1-methylimidazol-2-yl)methyl)amine) and BIPA (bis(1-methylimidazol-2-yl)methyl)((2-pyridyl)methyl)amine) have been synthesized. These are close analogues of TMPA (=tris((2-pyridyl)methyl)amine), where we previously showed that $[(TMPA)Cu(RCN)]^+$ (**1a**) (R = Me, Et) reacts (−80 °C) with O_2 reversibly, to form the *trans*-(μ-1,2-peroxo)dicopper(II) complex $[\{(TMPA)Cu\}_2(O_2)]^{2+}$ (**1b**). Copper(I) complexes of BPIA and BIPA have been synthesized, and the X-ray structure of $[(BPIA)_2Cu_2]^{2+}$ (**2a′**) was determined; for $C_{36}H_{36}Cu_2F_6N_{10}O_6S_2$, $a = b = 14.057(4)$ Å, $c = 41.755(6)$ Å, tetragonal space group $I\bar{4}2d$, and $Z = 8$. The structure is a dimer, and each Cu(I) ion is coordinated in a trigonal pyramidal N_4 environment. Dinuclear complex formation comes about as a result of ligation of the imidazolyl group of the BPIA donor to the adjacent Cu(I) ion. Conductivity measurements reveal that the cuprous complexes are mononuclear in nitrile or dimethylformamide solvents, thus formulated as $[(BPIA)Cu(S)]^+$ (**2a**) and $[(BIPA)Cu(S)]^+$ (**3a**) (S = solvent). Substitution of one or two imidazolyl donors for pyridyl groups in **1a**, on going to **2a** or **3a**, has little effect on redox properties. Cyclic voltammetry measurements indicate that **1a**–**3a** undergo quasi-reversible one-electron oxidation processes, occurring close to −600 mV versus $Ag/AgNO_3$. Low-temperature (−80 °C) oxygenation of **2a** does result in the generation of a stable dioxygen adduct, formulated as $[\{(BPIA)Cu\}_2(O_2)]^{2+}$ (**2b**) on the basis of manometric measurements (Cu/O_2 = 2:1 in EtCN at −80 °C), its EPR silence, and the close similarity of its UV–vis spectrum (λ_{max} = 535 nm, ϵ = 11 500 $M^{-1}\,cm^{-1}$) compared to that of **1b**. By contrast, **3a** reacts rapidly with O_2 at −80 °C to give an intensely red-colored solution (λ_{max} = 330 nm), but the putative O_2 adduct is unstable, as judged by the bleaching of the solution within minutes. The results are compared to ligand/copper complex systems containing pyridyl and/or quinolyl donors.

Introduction

Our efforts in functional modeling of copper proteins which interact with or activate dioxygen (O_2)[1,2] have included the study of O_2 reactivity with $[(TMPA)Cu(RCN)]^+$ (**1a**) (R = Me, Et).[3–6] TMPA is the tripodal tetradentate ligand tris((2-pyridyl)methyl)amine, and **1a** is a pentacoordinate Cu(I) species (with a long Cu–$N_{tert\text{-}amine}$ interaction) which gives the *trans*-(μ-1,2-peroxo)dicopper(II) complex $[\{(TMPA)Cu\}_2(O_2)]^{2+}$ (**1b**) upon addition of O_2 at −80 °C.



$[(TMPA)Cu(RCN)]^+$ (1a) $[\{(TMPA)Cu\}_2(O_2)]^{2+}$ (**1b**)

Studies on system like this are of importance in the elucidation of structural, spectroscopic, and reactivity correlations in copper–dioxygen chemistry. Copper ion serves as a catalyst for oxidative conversions,[7–9] and our particular interests include very basic Cu(I) and Cu_n/O_2 reactivity of possible relevance to proteins such as hemocyanin (Hc), an anthropodal and molluscan O_2 carrier.[10–13] Dioxygen binding, followed by activation in as yet undetermined manners, allows for C–H oxidative processes in a variety of copper monooxygenases such as tyrosinase (Tyr) (*o*-hydroxylation of phenols),[11] peptidyl α-amidating monooxygenase (PAM; oxidative N-dealkylation of glycine-extended peptide prohormones),[14] and *particulate*-methane monooxygenase.[15] Dioxygen binding and reduction to hydrogen peroxide or water (i.e. O–O cleavage reactions) occurs in copper oxidases,[9,11] and thus the chemistry of O_2 binding to Cu(I) centers is also relevant to enzymes such as ascorbate oxidase (AO)[11,16] and cytochrome *c* oxidase (reducing O_2 at a dinuclear heme-iron/copper center).[17,18]

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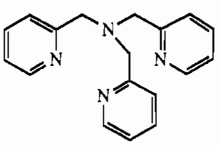
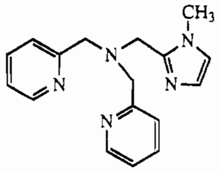
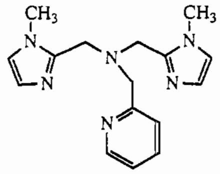
Chart 1



TMPA



BPIA



BIPA

The success with TMPA in generating a tractable dioxygen–copper adduct (e.g., $Cu_2O_2^{2+}$) has spurred us to make changes in this tripodal ligand, such as systematic substitution of a variable number of 2-pyridyl groups with 2-quinolyl donors. We find that copper(I) complexes with tripodal tetradentate ligands containing 2-quinolyl donor groups can also form stable copper dioxygen complexes but that the observed stoichiometry of reaction (i.e., Cu/O_2 = 1:1 or 2:1) and associated spectroscopy can be greatly affected by these ligand changes.[5,19]

Following these observations, we also have synthesized tripodal ligands and copper complexes with imidazolyl donor groups. The imidazolyl-containing tripodal ligands (L) used in the present study are BPIA (bis((2-pyridyl)methyl)(1-methylimidazol-2-yl)-methyl)amine) and BIPA (bis((1-methylimidazol-2-yl)methyl-((2-pyridyl)methyl)amine), shown in Chart 1. Buchanan and co-workers[20] have reported alternate synthesis of these particular imidazolyl-containing ligands and investigations of their copper(II) complexes. However, neither copper(I) complexes with these ligands nor copper(I)–dioxygen chemistry has been otherwise studied. Here, we report the synthesis and characterization of cuprous complexes with BPIA and BIPA. An X-ray crystal structure of the dinuclear complex $[(BPIA)_2Cu_2]^{2+}$ (**2a′**) is described, and comparisons of the electrochemical properties of the mononuclear solution species $[(BPIA)Cu]^+$ (**2a**) and $[(BIPA)Cu]^+$ (**3a**)[21] and the parent compound $[(TMPA)Cu(RCN)]^+$ (**1a**) are made. The reaction of these Cu(I) complexes with dioxygen at low temperature (−80 °C) are also detailed.

Model systems containing imidazole donor ligands are of special interest, as histidine-to-copper ligation pervades copper biochemistry,[22] including the active sites of Hc, Tyr, dopamine-β-hydroxylase,[23,24] galactose oxidase,[25,26] ascorbate oxidase,[11,16] and superoxide dismutase.[27] Investigations of copper(I)–dioxygen chemistry in imidazolyl-containing ligand environments are important, in (i) understanding the special role of such donors compared to others, (ii) elucidating effects of ligand basicity and/or π-bonding, N^{δ} versus N^{ϵ} coordination, and hydrogen bonding to the uncoordinated imidazole nitrogen (e.g., from peptide backbone groups), and (iii) affording the possibility of more closely mimicking biological structures and spectroscopic properties. A number of other researchers have utilized imidazoles or polyimidazole-containing chelating ligands in studies of copper coordination chemistry and or Cu(I)–dioxygen reactivity.[28–35]

Results and Discussion

General Synthesis of Cu(I) Complexes. The procedure for the synthesis of copper(I) complexes with BPIA and BIPA follows that established for the TMPA ligand, which has three pyridyl donors,[4] consisting of adding 1 equiv of appropriate tripodal ligand and $[Cu(CH_3CN)_4]Y$ ($Y = ClO_4^-, CF_3SO_3^-$) in acetonitrile under argon. As solids, these new compounds are dimeric, i.e., $[(BPIA)_2Cu_2]^{2+}$ (**2a′**) and $[(BIPA)_2Cu_2]^{2+}$ (**3a′**), as determined by X-ray crystallography for **2a′**. However, when **2a′** and **3a′** are redissolved in MeCN or EtCN solution, they dissociate and conductivity measurements[36] (see also Experimental Section) reveal that these are mononuclear, formulated as $[LCu(RCN)]^+$ (vide infra).

$$2[Cu(CH_3CN)_4]Y + 2L \text{ (tripodal ligands)} \rightarrow [(L)_2Cu_2]Y_2$$

as solids

2a′ (L = BPIA)

3a′ (L = BIPA)

$$Y = CF_3SO_3^- \text{ or } ClO_4^-$$

The synthesis and handling or study of the Cu(I) complexes must be carried out exclusively in organonitrile solvents. Use of dichloromethane, which is generally useful in the study of copper(I)–dioxygen chemistry,[37] is not possible, since both $[L_2Cu_2]^{2+}$ (**2a′**, **3a′**) complexes react rapidly with CH_2Cl_2. This same behavior is also observed for the parent complex $[(TMPA)Cu(RCN)]^+$ (**1a**).[4] Abstraction of chlorine occurs, and chloride–Cu(II) complexes $[LCuCl]^+$ form in high yield. In a separate study, we showed that $[(TMPA)Cu(RCN)]^+$ (**1a**) is efficient in reductive coupling of organic halide compounds,[38] while Maverick

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Table 1. Crystallographic Data for $[(BPIA)_2Cu_2](CF_3SO_3)_2$ (**2a**′$(CF_3SO_3)_2$)

formula	$C_{36}H_{36}Cu_2$-$F_6N_{10}O_6S_2$	D_{calcd}, g/cm^3	1.63
		space group	$I\bar{4}2d$ (No. 122)
MW	1011.96		
cryst system	tetragonal	refcns collcd	2138
$a = b$, Å	14.057(4)	reflcns used	1452
c, Å	41.755(6)	abs coeff, cm^{-1}	7.76
$\alpha = \beta = \gamma$, deg	90.00	no. of refined params	280
V, Å^3	8251(4)	largest peak/hole, e Å^{-3}	0.53/–0.38
Z	8	R^a	0.050
$F(000)$	4112	$R_w{}^b$	0.068

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

Table 2. Positional Parameters and B(eq) Values for **2a**′$(CF_3SO_3)_2$

atom	x	y	z	B(eq)
Cu1	0.2410(1)	0.1345(1)	0.13380(3)	3.43(6)
S1	0.3487(3)	0.2423(2)	0.45807(7)	5.1(2)
F1	0.4409(7)	0.3468(8)	0.4987(2)	9.4(6)
F2	0.410(1)	0.4125(9)	0.4556(3)	14(1)
F3	0.5138(8)	0.314(1)	0.4557(4)	18(1)
O1	0.3489(8)	0.2379(7)	0.4250(2)	6.6(5)
O2	0.2664(8)	0.276(1)	0.4731(3)	10.6(8)
O3	0.384(2)	0.1637(8)	0.4733(2)	14(1)
N1	0.2418(7)	0.1765(5)	0.1874(2)	2.7(4)
N2	0.1009(6)	0.1286(6)	0.1423(2)	3.1(4)
N3	0.3139(7)	0.0144(6)	0.1593(2)	3.3(4)
N4	0.3361(6)	0.1506(6)	0.1005(2)	3.0(4)
N5	0.4059(6)	0.1522(7)	0.0533(2)	3.5(4)
C1	0.434(1)	0.333(1)	0.4677(4)	6(1)
C21	0.0324(8)	0.124(1)	0.1199(3)	4.3(6)
C22	–0.0627(8)	0.133(1)	0.1269(3)	5.2(6)
C23	–0.0880(8)	0.146(1)	0.1595(4)	6.0(8)
C24	–0.0191(8)	0.152(1)	0.1817(3)	4.5(6)
C25	0.0742(7)	0.1412(8)	0.1727(3)	3.3(5)
C26	0.1517(8)	0.133(1)	0.1975(2)	3.5(5)
C31	0.332(1)	–0.0714(9)	0.1470(3)	4.2(6)
C32	0.3730(8)	–0.1448(9)	0.1644(3)	4.4(6)
C33	0.395(1)	–0.128(1)	0.1957(3)	4.9(7)
C34	0.376(1)	–0.0391(9)	0.2085(3)	4.0(6)
C35	0.3368(8)	0.0296(8)	0.1904(2)	3.4(5)
C36	0.3214(8)	0.1299(8)	0.2028(2)	3.4(5)
C41	0.4279(8)	0.1194(9)	0.1034(3)	3.7(5)
C42	0.4721(8)	0.1191(8)	0.0743(3)	4.0(6)
C43	0.3250(8)	0.1734(7)	0.0693(2)	2.4(4)
C44	0.419(1)	0.154(1)	0.0190(3)	4.7(6)
C45	0.2386(9)	0.2808(7)	0.1934(2)	3.1(5)

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[(BPIA)_2Cu_2](CF_3SO_3)_2$ (**2a**′$(CF_3SO_3)_2$)

	Bond Distances		
Cu1–N1	2.315(8)	Cu1–N3	2.243(9)
Cu1–N2	2.003(9)	Cu1–N4	1.941(8)
	Bond Angles		
N1–Cu1–N2	81.0(3)	N2–Cu1–N3	109.5(3)
N1–Cu1–N3	74.4(3)	N2–Cu1–N4	144.0(3)
N1–Cu1–N4	131.2(3)	N3–Cu1–N4	96.5(3)

and co-workers have observed the nucleophilic attack of a Cu(II) complex on CH_2Cl_2, producing chloro–copper(II) species.[39]

X-ray Structure of $[(BPIA)_2Cu_2](CF_3SO_3)_2$ (2a′$(CF_3SO_3)_2$). X-ray-quality yellow block-shaped crystals of $[(BPIA)_2Cu_2](CF_3SO_3)_2$ were obtained by recrystallizing the Cu(I) complex from acetonitrile/diethyl ether. The complex crystallizes in the unusual tetragonal space group $I\bar{4}2d$. A summary of crystal data and refinement parameters of this complex is given in Table 1. Final coordinates and thermal parameters are given in Table 2, while selected bond distances and angles are listed in Table 3.

Complex **2a**′ is a dimeric, $[(BPIA)_2Cu_2]^{2+}$, as shown in Figure 1. The Cu(I) complex dimer is formed by a sharing of the two BPIA ligands. Each tetracoordinated copper(I) ion is ligated with two pyridyl nitrogen atoms and one tertiary amine nitrogen atom of a single BPIA ligand, with the fourth coordinating atom from the imidazole nitrogen of the second adjacent tripodal BPIA ligand. In the structure, the two copper(I) ions are separated by 3.229(3) Å. Due to the 2-fold symmetry, each Cu(I) ion is in an identical environment. The geometry about Cu(I) is a distorted trigonal pyramidal. Atoms N1, N2, and N4 form the basal plane, and Cu1 lies 0.21 Å away from it toward the axial N3 atom. Relevant dihedral angles are Cu1–N1–N2/Cu1–N3–N4 = 116.47° and Cu1–N2–N4/Cu1–N1–N3 = 114.83°. The "hard" amine nitrogen N1 bonds more weakly to the Cu(I) ion (Cu1–N1 = 2.315(8) Å) compared to the other three N atoms originating from the pyridyl or imidazolyl donors (Cu–N = 1.94–2.24 Å). The Cu1–N2 (2.003(9) Å) distance is normal and falls in the range of typical Cu–N(py) distances of tetracoordinated Cu(I) complexes (2.0–2.05 Å), while the axial bond Cu1–N3 (2.243(9) Å) is rather longer. The Cu–N(im) (Cu–N4) distance 1.941(8) Å is shorter than typical Cu–N(py) distances but is in the range of those observed for a Cu(I) dimer with tripodal tricoordinate imidazole ligands reported by Sorrell (Cu–N(im) = 1.90–2.04 Å).[29] For five-coordinate $[LCu^{II}Cl]^+$ complexes with BPIA or BIPA, Cu–N(im) distances in the range 2.01–2.06 Å are observed.[20]

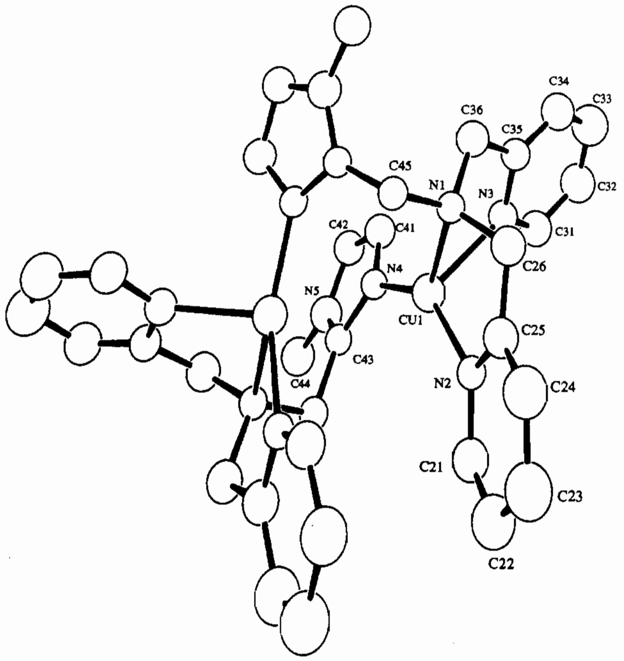

Figure 1. ORTEP diagram of the cationic portion of $[(BPIA)_2Cu_2]^{2+}$ (**2a**′), showing the atom-labeling scheme.

The dimeric structure observed for $[(BPIA)_2Cu_2]^{2+}$ (**2a**′) contrasts with that seen for copper(I) complexes with somewhat similar tripodal tetradentate ligands, such as TMPA, TEPA, (TEPA = tris((2-pyridyl)ethyl)amine), and quinolyl-containing analogs,[19] where only mononuclear complexes were isolated and structurally characterized. One possible driving force for the dimerization of this copper(I) complex **2a**′ might be a stacking interaction between two pyridine rings of the two BPIA ligands in the dimer complex. Two pyridyl rings of the two separate BPIA tripodal ligands lie essentially on top of each other (in a staggered fashion), with the average ring to ring distance ~3.5 Å. The two rings are tilted with respect to each other by 6.8°. A figure showing this stacking interaction is given in the supplementary material. A very similar kind of stacking interaction is also observed between pyridine rings in copper(II) complexes with pyridyl-containing ligands, i.e., $[(Cu(TMPA)(F)]_2{}^{2+}$ [40] and $[Cu(BPY2)(OH)_2{}^{2+}$ [41,42] [BPY2 = bis((2-pyridyl)ethyl)benzylamine)].

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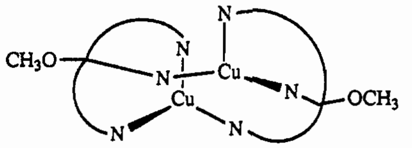
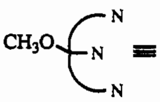
Sorrell has described a structurally similar dinuclear copper(I) complex $[(\text{timm})_2\text{Cu}^{\text{I}}_2]^{2+}$ utilizing a tridentate imidazolyl complex with the tris[2-(1-methylimidazolyl)]methoxymethane (timm) ligand. Here, sharing one imidazole donor group of a ligand with a second copper ion occurs as shown. Unlike what we observe for $[(\text{BPIA})_2\text{Cu}_2]^{2+}$ (**2a′**) (vide infra), Sorrell's complex is unreactive toward dioxygen, even in methanol solution where this dimeric structure breaks down and mononuclear species are present.[29,43] More recently, Sorrell reported a dinuclear three-coordinate Cu(I) complex with a new tripodal tris(oxazoline) ligand, and it also forms a dimeric structure in a similar manner, i.e., sharing of nitrogen donors from one ligand between the two Cu(I) ions.[44] Tolman and co-workers also reported that a dimer copper(I) complex $\{[\text{HB}(t\text{-Bupz})_3]\text{Cu}\}_2$ forms when $\text{Tl}[\text{HB}(t\text{-Bupz})_3]$ [$\text{HB}(t\text{-Bupz})_3$ = hydrotris(3-*tert*-butyl-1-pyrazolyl)borate] reacts with CuCl in THF solvent.[45] This species has a linear two-coordinate N–Cu(I)–N structure, again by sharing of donors from different ligands. When a hydrotris(3,5-diphenylpyrazolylborate) ligand was used by the same research group, a dinuclear three-coordinate complex was structurally characterized.[46]



$[(\text{timm})_2\text{Cu}^{\text{I}}_2]^{2+}$



≡ tris[2-(1-methylimidazolyl)]methoxymethane

Solution Behavior and Electrochemistry. In acetonitrile and dimethylformamide (DMF), complexes **2a′** and **3a′** dissociate into mononuclear species, as determined from solution conductometric measurements. Recall also that Sorrell's dinuclear complex $[(\text{timm})_2\text{Cu}^{\text{I}}_2]^{2+}$ dissociates in polar media (i.e., methanol) and is presumed to exist as a solvent complex $[(\text{timm})\text{Cu}(\text{MeOH})]^+$.[29] Thus, complex **2a′** and **3a′** are formulated as solvent complexes $[(\text{BPIA})\text{Cu}]^+$ (**2a**) and $[(\text{BIPA})\text{Cu}]^+$ (**3a**), respectively, in either DMF or RCN (R = Me, Et) solution media,[21] in close analogy to the well-characterized complexes possessing the structurally similar TMPA ligand, $[(\text{TMPA})\text{Cu}(\text{RCN})]^+$ (**1a**) and $[(\text{TMPA}')\text{Cu}(\text{CH}_3\text{CN})]^+$ (where TMPA′ possesses a –C(O)Me ester group attached to the 5-position of one pyridyl ring of TMPA).[4]

The electrochemical behavior of cuprous complexes **1a**–**3a** was measured by cyclic voltammetry (CV) under argon in DMF, and the results are given in Table 4. All copper complexes displayed a single quasi-reversible one-electron redox behavior with $i_{\text{pa}}/i_{\text{pc}}$ = 0.80–0.95. Peak separations were less than 120 mV at a scan rate of 100 mV/s. The ferrocene/ferrocenium couple under the same conditions showed ΔE_{p} = 89 mV and $E_{1/2}$ = 20 mV versus Ag/AgNO_3. A typical CV scan for $[(\text{BIPA})\text{Cu}]^+$ (**3a**) is given in Figure 2. Results from bulk electrolysis experiments (Experimental Section) correspond to a one-electron process per copper complex; these experiments were accompanied by a color change from yellow (e.g., Cu(I) complex) to blue-green (e.g., oxidized Cu(II) species). The CV of a coulometrically oxidized solution gave the exact complement as that of the original Cu(I) complex solution at the same scan rate.

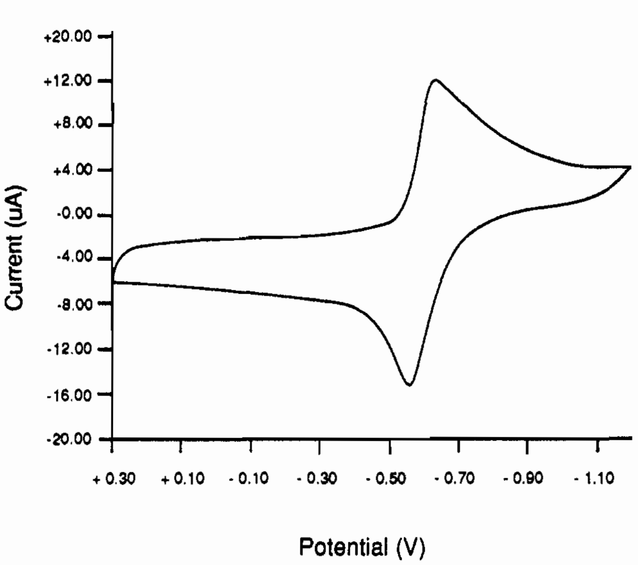


Figure 2. Cyclic voltammogram of $[(\text{BIPA})\text{Cu}]^{3+}$ (**3a**) in DMF at room temperature.

Table 4. Cyclic Voltammetry Data for Cu(I) Complexes in DMF

complexes	$E_{1/2}$, mV	ΔE_{p}, mV	$i_{\text{pa}}/i_{\text{pc}}$
$[(\text{TMPA})\text{Cu}(\text{RCN})]^+$ (**1a**)	–608	78	0.80
$[(\text{BPIA})\text{Cu}]^+$ (**2a**)	–603	112	0.80
$[(\text{BIPA})\text{Cu}]^+$ (**3a**)	–595	69	0.95

From Table 4, we see that the $E_{1/2}$ values for **2a** and **3a** are very close to that of the parent $[(\text{TMPA})\text{Cu}(\text{RCN})]^+$ complex (**1a**). While there appears to be a slight trend toward more positive $E_{1/2}$ values when the ligand contains more imidazolyl groups, we cannot conclude that any significant differences exist. There are many factors which are known to influence the redox potentials of copper complexes including (a) the flexibility or constraints imposed by chelating ligands, (b) the types of donor atoms, and (c) the geometry in tetracoordinate complexes. According to HSAB theory, imidazole is a pseudo-aromatic molecule and a borderline base.[20,47] It is a stronger base than pyridine ($\text{p}K_{\text{b}}$ = 6.95 for imidazole, $\text{p}K_{\text{b}}$ = 8.74 for pyridine) but softer compared to pyridine. In aqueous solution, it has also been reported that the Cu(II)/Cu(I) couple with simple imidazolyl ligands has a more positive $E°$ value than with pyridyl donors (e.g., $E°$ = 0.348 V for imidazole and $E°$ = 0.270 V for pyridine).[48–50] Therefore, ligands containing imidazolyl donor groups favor Cu(I). Thus, we would have expected that $E_{1/2}$ values become more positive as the tripodal ligand becomes progressively softer (i.e., TMPA < BPIA < BIPA), but little difference in Cu(II)/Cu(I) redox potentials for **1a**–**3a** is observed (Table IV). Buchanan and coworkers studied the electrochemistry of Cu(II) complexes with the same exact ligands, i.e., $[\text{LCu}^{\text{II}}(\text{Cl})]^+$; they also observed surprisingly small differences in redox potential upon imidazolyl substitution for pyridyl donors, although the trend was more in the direction expected (in CH_3CN, $E_{1/2}$ = –0.273 V for BPIA and –0.207 V for BIPA versus NHE).[20]

Low-Temperature Reactions of O_2 with Copper(I) Complexes 2a and 3a. When a yellow propionitrile solution of Cu(I) complex $[(\text{BPIA})\text{Cu}]^+$ (**2a**) was oxygenated at –80 °C, an immediate reaction took place, resulting in the formation of an intense purple species. Manometric measurements for **2a** at –80 °C were carried

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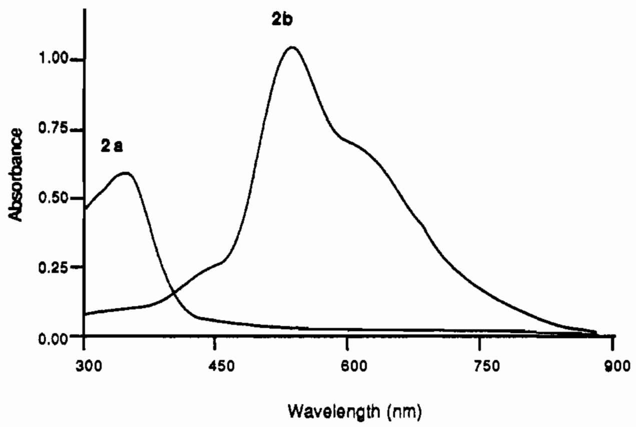


Figure 3. Low-temperature UV–vis spectra of [(BPIA)Cu]$^+$ (**2a**) and [{(BPIA)Cu}$_2$(O$_2$)]$^{2+}$ (**2b**).

Table 5. UV–Vis Spectral Data for Cu(I) Complexes and Their Dioxygen Complexes in EtCN

Cu^I complexes	Cu^I band λ_{max}, nm (ϵ, M^{-1} cm^{-1})	bands for (LCu)$_2$–O$_2$ complexes **1b**–**3b** λ_{max}, (ϵ, M^{-1} cm^{-1})
[(TMPA)Cu(RCN)]$^+$ (**1a**)	343 (5600)	525 (11 500), 590 (7600), 440 (4000), 1035 (160)
[(BPIA)Cu]$^+$ (**2a**)	348 (3000)	535 (11 500), 600 (7600), 440 (2000)
[(BIPA)Cu]$^+$ (**3a**)	320 (1300)	330 (1500)^a 500 (510)^a

^{a} Putative unstable Cu$_2$O$_2$ complex; see text.

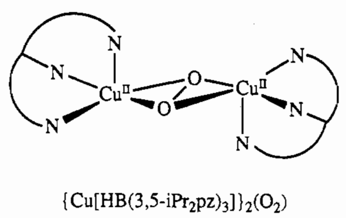
out in order to determine the stoichiometry of the reaction with O$_2$. The results show that the absorption of dioxygen by [(BPIA)-Cu]$^+$ (**2a**) is in the ratio of Cu/O$_2$ = 1.90 (±0.05):1, consistent with a [{(BPIA)Cu}$_2$(O$_2$)] (**2b**) formulation.

A low-temperature UV–vis spectrum of [{(BPIA)Cu}$_2$(O$_2$)]$^{2+}$ (**2b**) at −80 °C exhibits absorptions at λ_{max} 535 nm (ϵ = 11 500 M^{-1} cm^{-1}), ca. 440 nm (sh, ϵ = 2000 M^{-1} cm^{-1}), and ca. 600 nm (sh, ϵ = 7600 M^{-1} cm^{-1}), Figure 3 and Table 5. We suggest that the dioxygen adduct **2b** has the same structure as that determined for the TMPA-containing ligand, i.e., [{(TMPA)Cu}$_2$(O$_2$)]$^{2+}$ (**1b**), a *trans*-(μ-1,2 peroxo)dicopper(II) moiety, since there is a very close similarity of spectral features, both in band position and intensity (i.e., ϵ). For **1b**, a detailed spectroscopic investigation revealed that all of these strong bands can be assigned as O$_2{}^{2-}$-to-Cu(II) LMCT transitions.[6] Electron paramagnetic resonance measurements for **2b** at 77 K indicate it is EPR silent, consistent with the conclusion that the two Cu(II) ions in **2b** are magnetically coupled. This agrees with the Cu$_2$O$_2{}^{2+}$ formulation proposed, since O$_2{}^{2-}$ has two unpaired electrons and they can spin couple with two unpaired electrons coming from two Cu(II) ions. This is similar to complex **1b**, where $-2J$ has been measured and found to be >600 cm^{-1} ($\mathcal{H} = 2J S_1 \cdot S_2$).[51] Several attempts were made to carry out low-temperature (−80 °C) ^{1}H NMR spectroscopic studies on **2b**; however, due to handling and technical problems, these were not successful.

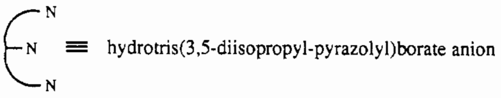
Through a detailed low-temperature spectroscopic investigation,[5,19] we similarly observed that the cuprous complex [(BPQA)Cu]$^+$ [BPQA = bis((2-pyridyl)methyl)((2-quinolyl)-methyl)amine], where one pyridyl donor of the TMPA ligand is substituted by a 2-quinolyl donor group, reacts with O$_2$ to give a Cu/O$_2$ = 2:1 Cu$_2$O$_2{}^{2+}$ adduct [{(BPQA)Cu}$_2$(O$_2$)]$^{2+}$, also exhibiting spectral features nearly identical to those seen for **1b**. These observations indicate that when one pyridyl group of the TMPA ligand is substituted by either a quinolyl or an imidazolyl donor, the environment about the Cu(I) center is sterically and electronically similar.

It should be noted that the complete kinetic study[5] indicates that oxygenation of [(TMPA)Cu]$^+$ (**1a**) proceeds via the formation of a Cu/O$_2$ = 1:1 adduct, i.e., [(TMPA)Cu(O$_2$)]$^+$, which then further reacts with **1a** present in solution to give the final 2:1 adduct [{(TMPA)Cu}$_2$(O$_2$)]$^{2+}$ (**1b**). It is reasonable to assume that [{(BPIA)Cu}$_2$(O$_2$)]$^{2+}$ (**2b**) forms through a similar reaction mechanism, but our bench-top spectroscopic measurements (Experimental Section) preclude observation of transiently formed species, such as a putative 1:1 intermediate adduct [(BPIA)Cu(O$_2$)]$^+$.

By contrast, when a solution of [(BIPA)Cu]$^+$ (**3a**) (~10^{-4} M) was exposed to dioxygen at −80 °C propionitrile solvent, the yellow color immediately changed to red, but the red species (or perhaps multiple products which are formed) is not stable even at this temperature and rapidly decomposes (i.e., in minutes), as judged by the spectral bleaching (i.e., severe loss of intensity) observed. This behavior also precluded the O$_2$-uptake measurements which would help to determine reaction stoichiometry. In any case, we recorded the spectrum of the red solution with λ_{max} = 330 nm (Figure 4). Molar extinction coefficients recorded (Table 5) were calculated on the basis of the most intense peaks obtainable (e.g., by reading the maximum absorption of the spectrum of oxygenated species) with the assumption that it is a copper–dioxygen [Cu$_2$O$_2$]$^{2+}$ complex **3b**. The intensity of the peaks observed for a putative unstable dioxygen adduct **3b** are rather low compared to those often seen for copper–dioxygen complexes,[4] including **1b** and **2b** (Table 5). This may be due to the instability of **3b**, since it is likely that the maximum absorption of this initially observed spectrum corresponds to a species already largely decomposed. However, it is interesting to note that the UV–vis spectral pattern observed here is rather similar to that reported for the side-on μ-η^2:η^2 peroxide-bridged cupric dimer {Cu[HB(3,5-R$_2$pz)$_3$]}$_2$(O$_2$), described by Kitajima and co-workers (λ_{max} 338 nm, ϵ = 20 800 M^{-1} cm^{-1}; 530 nm, ϵ = 840 M^{-1} cm^{-1}).[2,52] This indicates that a metastable copper–dioxygen complex **3b** might have a similar copper–peroxo binding configuration.



{Cu[HB(3,5-iPr$_2$pz)$_3$]}$_2$(O$_2$)



The quite different UV–vis spectrum of **3b** also exhibits some similarity to the [(BQPA)Cu]$^+$ [BQPA = bis((2-quinolyl)-methyl)((2-pyridyl)methyl)amine] complex where two pyridyl groups of TMPA ligand are substituted by quinolyl donors and where a 1:1 CuO$_2$ adduct formed, e.g., [{BQPA)Cu}(O$_2$)]$^+$, with λ_{max} 378 nm, ϵ = 8200 M^{-1} cm^{-1}.[5,19] It is obvious that when two pyridyl groups are replaced by either quinolyl or imidazolyl groups, the steric and/or electronic environment about the Cu(I) center is very different from that of the parent [(TMPA)Cu(RCN)]$^+$ (**1a**) complex.

Conclusions

It is encouraging that copper(I) complexes can be formed with tripodal ligands containing potentially more biologically relevant imidazolyl donors. Upon reaction with O$_2$, copper–dioxygen complexes can be generated. Complex [(BPIA)Cu]$^+$ (**1a**)

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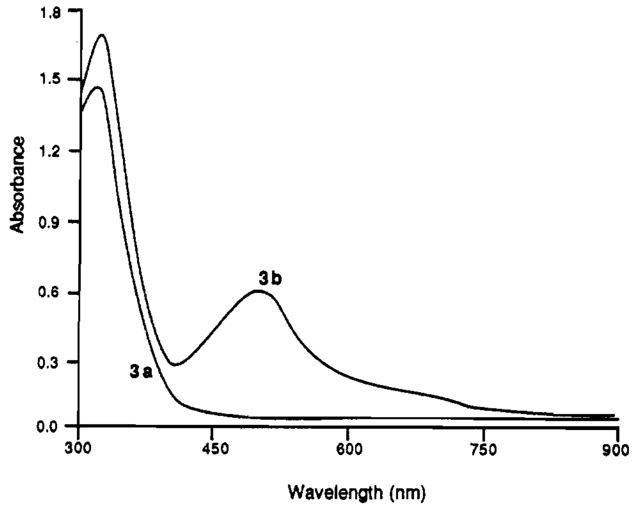

Figure 4. Low-temperature UV–vis spectra of $[(\mathrm{BIPA})\mathrm{Cu}]^+$ (**3a**) and $[\{(\mathrm{BIPA})\mathrm{Cu}\}_2(\mathrm{O}_2)]^{2+}$ (**3b**).

exhibited very similar copper–dioxygen chemistry and UV–vis spectroscopic features compared to the parent $[(\mathrm{TMPA})\mathrm{Cu}(\mathrm{RCN})]^+$ complex, as well as the quinolyl-containing $[(\mathrm{BPQA})\mathrm{Cu}]^+$ complex.[19] This indicates that when one of the three pyridyl rings is substituted by an imidazolyl or quinolyl donor, the steric and electronic environment around Cu(I) center is very similar. However, when two pyridine groups are substituted by two imidazole donors, the copper dioxygen chemistry is largely altered and the product(s) is (are) less stable. The reasons for this are of interest, and further investigations with modified imidazolyl-containing ligands are being pursued.

Experimental Section

Materials and Methods. Reagents and solvents used were of commercially available reagent quality unless otherwise stated. Dioxygen gas was dried over a short column of supported $\mathrm{P_4O_{10}}$ (Aquasorb, Mallinkrodt). Propionitrile was first distilled over $\mathrm{P_4O_{10}}$, then refluxed, and distilled from $\mathrm{CaH_2}$ under argon. Anhydrous diethyl ether was used by passing it through a 50 cm long column of activated alumina, or it was directly distilled from sodium/benzophenone under argon. All ligands were synthesized and characterized in the air, unless otherwise stated. Preparation and handling of air-sensitive materials were carried out under an argon atmosphere by using standard Schlenk techniques. Deoxygenation of solvents and solutions was effected by either repeated vacuum/purge cycles using argon or bubbling of argon (20 min) directly through the solution. Copper(I) solid samples were stored and transferred, and samples for NMR and IR spectra were prepared in a Vacuum/Atmospheres drybox filled with argon. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Infrared spectra were recorded using Nujol mulls on a Mattson Galaxy 4030 FT-IR spectrometer. NMR spectra were measured in $\mathrm{CDCl_3}$, $\mathrm{CD_3CN}$ on either a Varian (400-MHz) or a Bruker (300-MHz) spectrometer. All spectra were recorded in 5-mm-o.d. NMR tubes. Chemical shifts were reported as δ values downfield from an internal standard of $\mathrm{Me_4Si}$. Electron paramagnetic resonance (EPR) spectra were obtained in frozen solutions at 77 K with 4-mm-o.d. quartz tubes in a Varian E-4 Model spectrometer operating at X-band. The field was calibrated with a powder sample of diphenylpicrylhydrazyl (DPPH; $g = 2.0037$). The solvent used was propionitrile with concentration of copper complex at $\sim 10^{-3}$ M. The signal obtained was roughly integrated by comparing the intensity observed ($I = h_{1/2}(w_{1/2\mathrm{h}})^2$) with that of a known concentration of $[(\mathrm{TEPA})\mathrm{Cu}(\mathrm{Cl})]\mathrm{PF_6}$ in DMF.[53] Low-temperature electron spectroscopic studies were carried out by using a Hewlett-Packard 8452A diode array spectrometer driven by a Compaq Desk Pro 386S computer using software written by On-line Instrument Systems, Inc. The spectrometer was equipped with a variable-temperature dewar and a cuvette assembly as described elsewhere.[54]

Synthesis of Ligands. 2-(Hydroxymethyl)-1-methylimidazole. A mixture of 1-methylimidazole (82.04 g, 1.00 mol) and paraformaldehyde (60.11 g, 2.00 mol) in 200 mL of water was refluxed for 4 days. The mixture solution was cooled and concentrated *in vacuo*, and $\mathrm{CH_2Cl_2}$ (5 × 100 mL) was used to extract the product. The organic layer was collected and dried over $\mathrm{MgSO_4}$, and after filtering, $\mathrm{CH_2Cl_2}$ solvent was removed under reduced pressure to dryness. The solid obtained was recrystallized from chloroform giving 60.56 g (54% yield) of a white crystalline material. Mp: 112–116 °C. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 3.6 (s, 3 H, $\mathrm{CH_3}$–im), 4.4 (s, 2 H, $\mathrm{CH_2}$–OH), 4.7–5.3 (br, 1 H, OH), 5.8 (d, 1 H im), 6.5 (d, 1 H, im).

2-(Chloromethyl)-1-methylimidazole. At 0 °C, 2-(hydroxymethyl)-1-methylimidazole (14.45 g, 0.13 mol) dissolved in 170 mL of $\mathrm{CHCl_3}$ was added dropwise to a solution mixture of 55 mL of $\mathrm{SOCl_2}$ and 50 mL of $\mathrm{CHCl_3}$. The reaction mixture was then refluxed for 1 h followed by evaporation of the solution under reduced pressure to dryness. The resulting off-white solid was suspended in diethyl ether and stirred overnight. The ether was decanted, and the product was dried under vacuum to give 20.04 g (93%, yield) of an off-white product. Mp: 177–181 °C. ^{1}H NMR (DMSO): δ 3.50 (s, 3 H, $\mathrm{CH_3}$–im), 4.82 (s, 2 H, $\mathrm{CH_2}$–im), 7.21 (d, 2 H, im).

BPIA. 2-(Chloromethyl)-1-methylimidazole (5.01 g, 30 mmol) was suspended in 100 mL of $\mathrm{CH_2Cl_2}$ and cooled to 0 °C. To this solution was added dropwise bis(picolyl)amine (Nepera) (5.98 g, 30 mmol) in 15 mL of $\mathrm{CH_2Cl_2}$, followed by the addition of triethylamine (8.4 mL, 60 mmol) in 30 mL of $\mathrm{CH_2Cl_2}$. The reaction mixture was allowed to warm to room temperature and stirred for 48 h. The solution was washed with water (2 × 200 mL) and 7% NaOH solution (1 × 100 mL), and the organic phase was collected, dried over $\mathrm{MgSO_4}$, treated with activated charcoal, and then filtered. The resulting solution was concentrated *in vacuo* to give a dark brown oil, which was crystallized from diethyl ether giving 4.85 g (55%, yield) of light yellow final product. Mp: 90–92 °C. ^{1}H NMR ($\mathrm{CD_3CN}$): δ 2.46 (s, 3 H, $\mathrm{CH_3}$–im), 3.49 (s, 2 H, $\mathrm{CH_2}$–im), 3.74 (s, 4 H, $\mathrm{CH_2}$–py), 6.76 (d, 1 H, im), 6.87 (d, 1 H, im), 7.16–7.71 (m, 6 H), 8.47–8.49 (m, 2 H, 6 py).

BIPA. 2-(Chloromethyl)imidazole (10.02 g, 60 mmol) was suspended in 200 mL of $\mathrm{CH_2Cl_2}$ and cooled to 0 °C. To this solution was added dropwise 2-(methylamino)pyridine (3.11 g, 30 mmol) in 30 mL of $\mathrm{CH_2Cl_2}$ followed by the addition of triethylamine (16.72 g, 120 mmol) in 60 mL of $\mathrm{CH_2Cl_2}$. The reaction mixture was warmed to room temperature and was allowed to stir for 48 h. The product solution was washed with water (3 × 200 mL), the organic layer was collected, dried over $\mathrm{MgSO_4}$, and filtered, and the solvent was evaporated under reduced pressure. The resulting solid was recrystallized from $\mathrm{CCl_4}$ to give 1.68 g (18%, yield). ^{1}H NMR ($\mathrm{CD_3CN}$): δ 2.46 (s, 6 H, $\mathrm{CH_3}$–im), 3.49 (s, 2 H, $\mathrm{CH_2}$–im), 3.74 (s, 4 H, $\mathrm{CH_2}$–py), 6.76 (d, 2 H, im), 6.87 (d, 2 H, im), 7.20 (m, 2 H), 7.60 (m, 1 H), 8.47–8.49 (m, 1 H, 6 py).

Synthesis of Copper(I) Complexes. $[(\mathrm{BPIA})_2\mathrm{Cu}_2](\mathrm{CF_3SO_3})_2$ (2a($\mathrm{CF_3SO_3}$)$_2$). A 100-mL Schlenk flask was charged with $[\mathrm{Cu}(\mathrm{CH_3CN})_4]\mathrm{CF_3SO_3}$ (3.16 g, 8.38 mmol) and BPIA (2.51 g, 8.55 mmol). Acetonitrile (10 mL) was bubbled with argon for 20 min and added to the solid whereupon a golden-yellow solution formed. This was allowed to stir for 0.5 h, and then diethyl ether (85 mL) was added to precipitate a yellow powder. The solution was decanted, and the yellow microcrystalline product (3.8 g, 90% yield) was dried under vacuum for 2.5 h. Anal. Calcd for $\mathrm{CuC_{18}H_{19}N_5F_3SO_3}$: C, 42.73; H, 3.78; N, 13.84. Found: C, 43.00; H, 3.90; N, 14.07. ^{1}H NMR ($\mathrm{CD_3CN}$): δ 3.56 (s, 3 H, $\mathrm{CH_3}$, $\mathrm{CH_3}$–im), 4.06 (br, 6 H, 3 $\mathrm{CH_2}$), 6.77 (s, 1 H), 7.02 (s, 1 H), 7.28–7.34 (m, 4 H), 7.74–7.79 (m, 2 H), 8.52 (s, 2 H, 6 py). IR (Nujol, cm^{-1}): 1599 (s, C=C), 1258 (vs, $\mathrm{SO_3}$), 1026 (s, $\mathrm{SO_3}$), 1221 (s, $\mathrm{CF_3}$), 1163 (vs, $\mathrm{CF_3}$). X-ray-quality yellow cubic crystals were obtained by dissolving about 0.1 g of Cu(I) complex in 5–8 mL of dioxygen-free acetonitrile and then carefully layering the solution with diethyl ether; crystals developed in 2–3 days.

$[(\mathrm{BIPA})_2\mathrm{Cu}_2](\mathrm{ClO_4})_2\cdot{}^1/_2\mathrm{Et_2O}$ (3a($\mathrm{ClO_4}$)$_2$). Dioxygen-free $\mathrm{CH_3CN}$ (10 mL) was added dropwise to solids BIPA (0.149 g, 0.503 mmol) and $[\mathrm{Cu}(\mathrm{CH_3CN})_4]\mathrm{ClO_4}$ (0.163 g, 0.498 mmol) under argon. The solution immediately changed to light yellow, and this was allowed to stir under argon for 15 min. Diethyl ether (80 mL) was used to precipitate the yellow solid, which was then washed with ether three times and dried under vacuum for 2.5 h, giving 0.18 g of yellow microcrystalline material (80% yield). Anal. Calcd for $\mathrm{Cu_{17}H_{22.5}N_6ClO_{4.25}}$: C, 42.69; H, 4.71;

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N, 17.58. Found: C, 42.79; H, 4.39; N, 17.86. ^{1}H NMR (CD_3CN): δ 1.07 (t, Et_2O), 3.36 (q, Et_2O), 3.45 (s, 6 H, CH_3, CH_3–im), 4.19 (br, 6 H, 3 CH_2), 6.91–7.50 (m, 6 H), 7.78 (t, 1 H), 8.68 (br, 1 H). IR (Nujol, cm^{-1}): 1599 (s, C=C), 1080 (vs, ClO_4^-).

Caution! While we have had no problems with this compound, perchlorate salts are potentially explosive and should be handled with great care.

Methods to Generate ($(Cu_n–O_2)^{n+}$) Species. A dioxygen-free [(BPIA)Cu]$^+$ (**2a**) solution was cooled to −80 to −90 °C by using a methanol/liquid-nitrogen slush bath. It was oxygenated at low temperature by bubbling dry dioxygen directly through the solution for 2 min. [(BIPA)Cu]$^+$ (**3a**) was oxygenated in the same manner for ~1 min.

Gas (O_2) Uptake Manometry. O_2 adsorption for complex **2a** at −80 °C was monitored at constant pressure in a glass buret as previously described.[54,55] A 25-mL side-arm Schlenk flask containing a propionitrile solution of $[(BPIA)_2Cu_2](CF_3SO_3)_2$ (0.491 g, 0.485 mmol) was attached to the manometer system and cooled to −80 °C under argon. After evacuation of the flask for 1 h, the stopcock leading to the reaction flask was closed and the buret assembly was equilibrated to 1 atm of O_2 pressure. Once equilibrium was achieved, dioxygen was allowed to enter the reaction flask causing the solution to immediately change to deep purple. The volume of dioxygen taken up was 11.5 mL (after adjusting for a solvent-only "blank" run) corresponding to a Cu/O_2 ratio of 1.90 (±0.05):1.

Electrochemistry. Cyclic voltammetry and bulk electrolysis were carried out by using a Bioanalytical Systems BAS-100B Electrochemistry Analyzer driven by a Gateway 2000 386DX/33 computer using the software written by BAS. The cell consisted of a modification of a standard three-chambered design equipped for handling of air-sensitive solution by utilizing high-vacuum valves (Viton O-ring) seals. Either a platinum disk (BAS MF 2013) or a glassy-carbon electrode (GCE, BAS MF 2012) was used as the working electrode. The reference electrode was Ag$^+$/$AgNO_3$. The measurements were performed at room temperature in DMF solvent containing 0.2 M tetrabutylammonium hexafluorophosphate (TBAHP) and 10^{-3}–10^{-4} M copper complex deoxygenated by bubbling it thoroughly with argon. A bulk electrolysis experiment resulted in the passage of 0.97 mol of electrons/mol of [(BIPA)Cu]$^+$ (**3a**) complex.

Conductivity. Electrical conductivity measurements were carried out in acetonitrile with a Barnstead Model PM-70CB conductivity bridge and a YSI Model 3403 conductivity cell. The cell constant was determined by using the standard aqueous KCl solution. Studies with varying concentrations of **2a′** gave an Onsager plot with straight line having a slope $b = 1429$, close to that of a typical 1:1 electrolyte such as [(TMPA)CuCl]$^+$,[56] where $b = 1028$; however it is rather different from that of the 2:1 electrolyte $[(MePY2)Cu_2(OH)_2]^{2+}$,[57] where $b = 2384$.

X-ray Structure Determination of $[(BPIA)_2Cu_2](CF_3SO_3)_2$ (2a′($CF_3SO_3)_2$). Light yellow block-shaped crystals of **2a′**$(CF_3SO_3)_2$ suitable for X-ray crystallographic analysis were grown from CH_3CN solution by layering with diethyl ether. A crystal having approximate dimensions of 0.2 × 0.2 × 0.2 mm was mounted on a glass fiber. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $16.40 < 2\theta < 19.32°$, corresponded to a tetragonal cell. The data were collected at room temperature using the ω–2θ scan technique to a maximum 2θ value of 50.0°. ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.13° with a take-off angle of 6.0°. Scans of $(1.21 + 0.30 \tan \theta)°$ were made at a speed of 2.0°/min. Of the 2138 reflections collected 2137 were unique ($R_{int} = 0.046$). Azimuthal scans of several reflections indicated no need for absorption correction. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares refinement by using neutral-atom scattering factors. Anomolous dispersion terms were included in F_c, and the values for $\Delta f'$ and $\Delta f''$ were those of Cromer. The hydrogen atoms were included at calculated positions. The final cycle of full-matrix least-squares refinement was based on 1452 observed reflections ($I > 3.00\sigma(I)$). All measurements were made on a Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα radiation (λ(Mo Kα) = 0.710 73 Å), and all calculations were performed on a VAX 3520 computer using the TEXSAN crystallographic software package. The crystal data and positional parameters are listed in Tables 1 and 2, respectively.

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Supplementary Material Available: A PLUTO plot showing stacking interaction between pyridine rings (Figure S1) and listings (Tables S1–S6) of hydrogen atom positional and thermal parameters, anisotropic thermal parameters, bond lengths and angles, and plane calculations for **2a′**$(CF_3SO_3)_2$ (10 pages). Ordering information is given on any current masthead page.

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