Synthesis, Cyclic Voltammetry, and X-ray Crystal Structures of Copper(I) and Copper(II) Complexes of Tris((6-phenyl-2-pyridyl)methyl)amine (TPPA)

Chang-lin Chuang,[†] Kitae Lim,[†] Qiu Chen,[‡] Jon Zubieta,[‡] and James W. Canary*[,†]

Departments of Chemistry, New York University, New York, New York 10003, and Syracuse University, Syracuse, New York 13244

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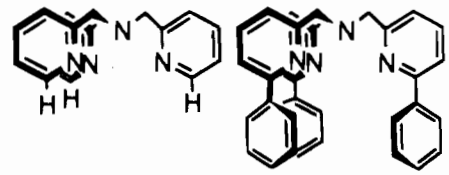
The synthesis and characterization of a new ligand, tris((6-phenyl-2-pyridyl)methyl)amine (TPPA) and some of its copper complexes are described. The complexes [Cu(TPPA)]BPh_4 (**7**) and [Cu(TPPA)(AN)]$(ClO_4)_2$ (**8**) (AN = acetonitrile) were prepared and their X-ray crystal structures and redox potentials were determined. The X-ray structure of **7** (triclinic space group, $P\bar{1}$; a = 14.603(3), b = 15.137(3), c = 12.974(3) Å, α = 91.76(3), β = 105.87(3), γ = 117.00(3)°, V = 2417.4(12) Å^3, Z = 2) displays a copper(I) atom with a distorted trigonal pyramidal coordination sphere, but the X-ray structure of **8** (triclinic space group, $P\bar{1}$; a = 13.458(3), b = 13.586(3) c = 11.082(2) Å, α = 113.00(3), β = 94.48(3), γ = 90.53(3)°, V = 1857.7(9) Å^3, Z = 2) indicates that the copper(II) atom has the expected trigonal bipyramid geometry. The reduction potential of **8** in dimethylformamide, dimethylacetamide, acetonitrile, and isobutyronitrile is quite positive compared to [Cu(TPA)]$(ClO_4)_2$ (TPA = tris(2-pyridylmethyl)amine) under identical conditions. The various factors that may contribute to the difference in oxidation potential are discussed. The positive redox potential combined with steric factors accounts for the lack of reactivity of [Cu(TPPA)]PF_6 with molecular O_2.

Introduction

The ligand tris(pyridylmethyl)amine (TPA, **1**) was first reported by Anderegg and Wenk in 1967.[1] Potentiometric studies on complexes of TPA with Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II), Hg(II), and Ag(I) have been reported.[2] Spectroscopic and/or crystallographic studies have also been reported for TPA complexes with V(IV),[3] Co(III),[4] Fe(III),[5,6] Mn(III),[7] Cu(I),[8] Cu(II),[9,10] Cd(II),[11] and Zn(II).[11,12] Copper[9] and iron[13] complexes of TPA have been used to model biological oxygen binding and activation. The ligand tris((6-methyl-2-pyridyl)methyl)amine has also been studied extensively[2] and has provided valuable information due to the steric hindrance provided by the three methyl substituents.[7,14,15] Recently, derivatives of TPA were reported in which 1, 2, or 3 pyridyl substituents were replaced by quinoline groups. The steric constraints of the ligand resulted in significant changes in the O_2 binding properties by Cu(I) complexes of the ligands.[16] A similar study that employed a derivative of TPA in which one of the pyridine substituents contains an attached carbomethoxy group was also reported recently.[17] Several other tripodal ligands have been studied in which the pyridyl groups are replaced by alternative heterocycles including imidazoles,[18] benzimidazoles,[19,20] and pyrazoles.[21,22]



1 (TPA) **2 (TPPA)**

The present paper is a first step toward the design and synthesis of Cu(II) complexes of synthetic TPA derivatives for molecular recognition studies.[23] The general idea is to use $[M(TPA)]^{n+}$ complexes as scaffolding to which organic functional groups can be attached for the development of synthetic

[†] New York University.
[‡] Syracuse University.
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receptors and enzyme mimics. Structural data on representative coordination complexes is critical for the design of such compounds. Our initial efforts in this area have focused on the synthesis of TPA analogs containing substituents in the 6-position of one or more pyridine rings (proximal to the available fifth coordination site in trigonal bipyramidal complexes).[23] The use of copper ions to organize the organic ligand allows an opportunity to "switch" the ligand between two different binding geometries. If the $[Cu(L)]^+$ and $[Cu(L)]^{2+}$ complexes display different ligand geometries, it may be possible to design electrochemical switches or chemical sensors based on the coordination complexes. Receptors,[24−27] vesicles,[28] and other supramolecular structures[29] activated or deactivated by means of redox changes have also been reported recently. In addition, several studies have appeared which describe noncovalent association of an organic molecule and a coordination complex in solution.[30−37]

Another possible interest in metal complexes of TPPA relates to the role of active-site amino acids in metalloproteins that contribute to binding and catalysis by means other than metal coordination. For example, recent studies of site-directed mutants of plastocyanin indicate that secondary interactions mediated by the protein strongly affect redox potential;[38] removal of hydrophobic side chains located near the copper atom in the protein makes the copper ion less easily reduced. The classical explanation of the unusually positive potentials of these metalloproteins reasons that the protein maintains the ligands in an enforced conformation, complementary to the copper(I) state; the oxidized state is thus distorted and consequently destabilized.[39] Both secondary interactions and metal/ligand coordination geometry play roles in the determination of the redox potential.

In order to uncover the coordination chemistry of copper complexes of 6-phenyl-substituted TPA derivatives and with the hope of obtaining information about the influence of hydrophobic ligand substituents on redox potentials in model compounds, ligand **2** was synthesized as well as its Cu(I) and Cu(II) complexes. The structures were studied both in the solid state and in solution, and the electrochemical behavior of the complexes was determined by cyclic voltammetry in acetonitrile (AN), isobutyronitrile (IBN), dimethylformamide (DMF), and dimethylacetamide (DMA).

Experimental Section

All reagents and solvents were purchased from commercial sources and used as received unless noted otherwise. The following were distilled under nitrogen before use: ether and tetrahydrofuran from sodium benzophenone ketyl; methanol from $Mg(OCH_3)_2$; DMF and DMA from sodium (distilled under reduced pressure); AN and IBN from CaH_2. Toluene was dried over activated molecular sieves. All chemical shifts are reported relative to an internal standard of TMS. Electroanalytical measurements were performed using an EG&G Model 273 potentiostat. GC/MS experiments were performed using a DB5 capillary GC column with a gradient program (100 °C for 1 min and increase 16 deg/min to 300 °C; He flow rate = 1 mL/min). ESI-MS experiments were performed on a Vestec Model 200 Electrospray mass spectrometer: needle voltage = 2.2 kV, ESI chamber temperature = 55 °C, repeller voltage = 200 V, lens temperature = 120 °C, block temperature = 250 °C, syringe pump injection (flow rate = 4 μL/min). Mass spectra are reported as the tallest peak of the isotope envelope with relative intensities in parentheses. UV−vis spectra were obtained on a Perkin-Elmer Lambda 5 instrument. The complex $[Cu(TPA)AN](ClO_4)_2$ (**9**) was synthesized as described[2] except that it was purified by recrystallization from methanol/ether. The presence of $[Cu(TPA)Cl](ClO_4)_2$ was verified by UV−vis spectroscopy since the latter complex shows a band at 330 nm.

6-Phenyl-2-pyridinecarboxaldehyde, 4. To a stirred solution of 6-bromopicolylaldehyde, **3**[40] (15.9 mmol, 2.96 g) and $Pd(PPh_3)_4$ (0.48 mmol, 0.55 g) in 32 mL of dry toluene under nitrogen was added 16 mL of 2 M Na_2CO_3(aq) and phenyl boronic acid (19.1 mmol, 2.33 g) in 10 mL of methanol.[41] The vigorously stirred mixture was refluxed for 8 h or until TLC indicated complete reaction. It was then allowed to cool and was partitioned between 100 mL of methylene chloride and 50 mL of 2 M sodium carbonate containing 5 mL of concentrated NH_3. The organic layer was dried (Na_2SO_4) and then concentrated under reduced pressure. Flash chromatography on silica gel (5:1 CH_2Cl_2:toluene) afforded **4** (2.11 g, 72.4%). ^1H NMR (200 MHz, $CDCl_3$): δ 10.1 (s), 8.3−8.1 (m), 8.1−8.0 (dd), 8.0−7.8 (d), 7.5−7.3 (m). MS (EI) *m/e*: 184.1 (9), 183.1 (61), 155.1 (64), 154 (100). IR (KBr, cm^{-1}): 1715 (s), 1580 (s), 1460 (s), 760 (s).

6-Phenyl-2-pyridinemethanol, 5. Compound **4** (50 mmol, 9.30 g) and $NaCNBH_3$ (55 mmol, 3.44 g) were dissolved in 75 mL of methanol.[42] A trace of methyl orange was added, and 2 N HCl−methanol was added dropwise with stirring, maintaining a red color. After the color changed very slowly, stirring was continued for 2 h. After removal of the solvent, the residue was taken up in 50 mL of water, saturated with sodium chloride, and extracted with three 75-mL portions of ether. The combined extracts were dried over Na_2SO_4, and the solvent was evaporated. Vacuum distillation gave compound **5** (8.29 g, 89.6%). ^1H NMR (200 MHz, $CDCl_3$): δ 8.1 (d), 7.8−7.4 (m), 4.8 (s). MS (EI) *m/e*: 186.1 (6.3), 185.1 (55), 184.1 (100). IR (KBr, cm^{-1}): 3500−3100 (br), 1650 (s), 1450 (s).

6-Phenyl-2-pyridinemethanamine, 6. Compound **5** (3.61 g, 19.1 mmol) was added to 20 mL of freshly distilled thionyl chloride in an ice bath. After the initial vigorous reaction had subsided, the reaction was refluxed for 2 h. The solution was cooled to room temperature, 30 mL of benzene was added, and the solution was allowed to stand for 20 min. The product precipitated from solution as a white solid. The solid was collected, washed several times with benzene, and dried to give 2-(chloromethyl)-6-phenylpyridine hydrochloride (4.12 g, 17.1 mmol, 90% yield). ^1H NMR (200 MHz, $CDCl_3$): δ 8.1 (d), 7.8−7.75 (dd), 7.7−7.65 (d), 7.55−7.4 (m), 4.4 (s). MS (free base form, EI) *m/e*: 206.1 (5), 205.1 (31), 204.1 (14), 203.1 (100), 168.2 (22), 167.1 (19).

The compound 2-(chloromethyl)-6-phenylpyridine hydrochloride (6.6 mmol, 1.59 g) in 10 mL of DMF was reacted with potassium phthalimide (7.34 mmol, 1.36 g) and sodium carbonate (7.34 mmol,

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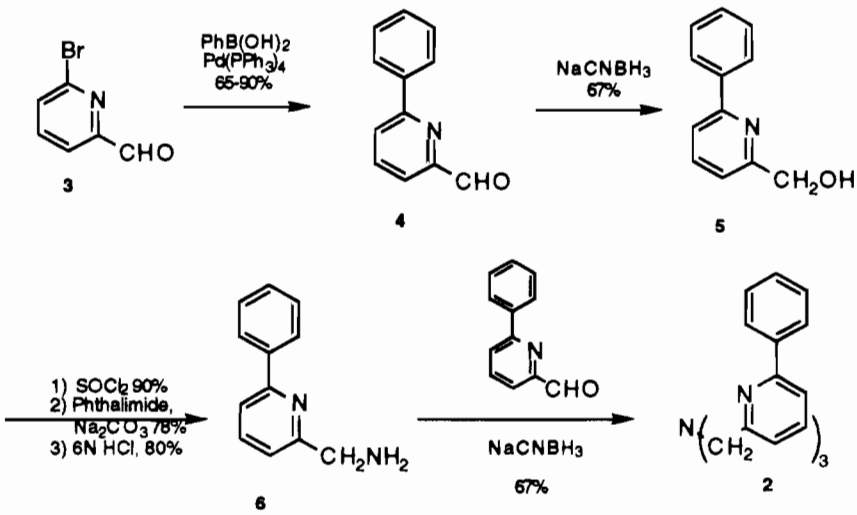

Figure 1. Synthesis of TPPA.

0.78 g). After the initial evolution of CO_2 subsided, the mixture was heated to reflux for 30 min. The mixture was cooled, and the salt was removed by filtration. The filtrate was concentrated to less than half its volume, and 20 mL of water was added. The white crystalline precipitate was collected. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.2−7.1 (m), 5.23 (s). MS (EI) *m/e*: 315.1 (23), 314.1 (100).

The solid, without further purification, was suspended in 20 mL of concentrated HCl and refluxed for 12 h. The resulting solution was cooled. The precipitate was removed by filtration and the filtrate was evaporated to dryness. Warm absolute ethanol (10 mL) was added to the residue and diluted with 20 mL of ether, and the white crystalline hydrochloride salt was collected, washed with ether, and dried. The free base was obtained by extraction using sodium bicarbonate from water and ether (yield 0.92 g, 76.5%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.1 (d), 7.8−7.2 (m), 4.1 (s), 2.2 (br s). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 162, 157, 140, 137, 129, 128, 126, 120, 118, 48.

Tris((6-phenyl-2-pyridyl)methyl)amine, 2. Compound **6** (450 mg, 2.43 mmol) in 10 mL of dry methanol was added to a solution of **4** (450 mg, 2.25 mmol) in 5 mL of methanol containing 0.2 mL of 6 M MeOH−HCl. The solution was allowed to stir for 36 h. $NaCNBH_3$ (305 mg, 4.86 mmol) was added. The solution was stirred for 3 h, when more **4** (890 mg) was added. The reaction was followed by TLC until complete consumption of **6** (if necessary, more **4** was added). A white precipitate formed as the reaction proceeded. Concentrated HCl was added until pH < 2 (5 mL) and the solvent was evaporated in vacuo. The residue was dissolved in 10 mL of water and extracted with three 5-mL portions of ether. The aqueous layer was basified with KOH until pH > 10 and extracted with three 10-mL portions of ether. The ether layer was dried over $MgSO_4$, and the solvent was removed. The crude tertiary amine was washed with ether and water. It was recrystallized from AN to yield white snowflakelike crystals (717 mg, 57%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.2−8.0 (d), 7.8−7.3 (m), 4.12 (s). ESI-MS *m/e*: 541 (150, M+Na$^+$), 519 (1478, M+H$^+$), 518 (1480). Anal. Calcd (mass %) for $C_{36}H_{30}N_4$: C, 83.36; H, 5.83; N, 10.80. Found: C, 83.12; H, 5.78; N, 10.86.

[Cu(TPPA)]BPh$_4$, 7. A protocol similar to one reported for a similar compound was followed.[43] A solution of $Cu(NO_3)_2(H_2O)_3$ (29.5 mg) in 2 mL of a 50% mixture of AN and water was added dropwise via pipet to a solution of TPPA (59.5 mg) in AN (5 mL). A solution of $NaBPh_4$ (150 mg) in 50% AN/water (2 mL) was added dropwise to the green solution. Within minutes of standing at ambient temperature, a yellow precipitate began to form. After 3 h, the solution was clear and the precipitate had turned to a green color. The green precipitate was collected, washed with water, and redissolved in AN (5 mL). An additional solution of $NaBPh_4$ (100 mg) in 50% AN/water was added. When this mixture was allowed to stand (under nitrogen) for several days, yellow crystals formed. The crystals, which were stable to air oxidation, were isolated and washed with water (mp 136−138 °C). The yield of **7** was 64%. Anal. Calcd (mass %) for $CuBC_{60}H_{50}N_4 \cdot C_2H_3N$: C, 79.01; H, 5.67; N, 7.43. Found: C, 79.40; H, 5.36; N, 7.40. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.77−7.69 (m), 7.58−7.51 (m), 7.16 (dd, $J_{1,2} = J_{2,3} = 5.0$ Hz), 7.08−7.01 (m), 6.86 (dd, $J_{1,2} = J_{2,3} = 4.6$ Hz), 6.66 (dd, $J_{1,2} = J_{2,3} = 5.0$ Hz), 3.67 (s).

[Cu(TPPA)(AN)](ClO$_4$)$_2$, 8. (***Caution!*** Perchlorate salts of metal complexes with organic ligands are potentially explosive. They should be handled in small quantity and with caution.)[44] A solution of $Cu(ClO_4)_2$ (50.3 mg) in water (2 mL) was added dropwise via pipet to a solution of tris((6-phenyl-2-pyridyl)methyl)amine (63.9 mg) in AN (7 mL). When the mixture was allowed to stand at ambient temperature, green crystals suitable for X-ray diffraction formed. The rate of precipitation could be accelerated by dilution of the solution with water. The yield of **8** was 60−80%. Anal. Calcd (mass %) for $C_{36}H_{30}N_4CuCl_2O_8 \cdot 0.5C_2H_3N$: C, 55.43; H, 3.96; N, 7.86. Found: C, 55.10; H, 3.70; N, 7.85. UV-vis (AN): λ_{max} (ϵ, M^{-1} cm^{-1}) = 855 (440), 304 nm (8100).

Cyclic voltammetry experiments were carried out in a standard three-electrode apparatus with a glassy carbon working electrode, a non-aqueous reference electrode (0.1 M $AgNO_3$ in acetonitrile), and a Pt wire auxiliary electrode. Experiments were run in 0.1 M tetrabutyl ammonium hexafluorophosphate as supporting electrolyte in DMF, DMA, AN, or IBN with scan rates of 50 or 100 mV. The complexes all undergo quasi-reversible one-electron reduction with current ratios i_c/i_a approaching unity. The electrochemical experiments were repeated, and the position of the waves was compared to the potential of the ferrocenium/ferrocene (Fc^+/Fc, E° = 0.4 V vs NHE) couple.

Results and Discussion

Synthesis. The synthesis of TPA (**1**) requires one step from 2-(aminomethyl) pyridine and 2-picolyl chloride (60−80% yield) in a concentrated solution of sodium hydroxide.[45] The preferential formation of the tertiary amine without quaternary ammonium formation appears to be at least in part due to templation by sodium ion, which the ligand is known to bind.[46] Few synthetic derivatives of TPA have been prepared,[2,16] possibly in part because of the restrictive reaction conditions used to prepare the parent compound. Indeed, our first attempts at the synthesis of TPPA (**2**) failed due to low solubility of the reagents in water. The successful synthesis utilized a reductive amination reaction[42] as the final step since methanol could be employed as solvent.

Compound **2** was prepared (Figure 1) beginning with the Suzuki coupling[47,48] of aldehyde **3** with phenylboronic acid to form biaryl **4**. The primary amine **6** was prepared via the

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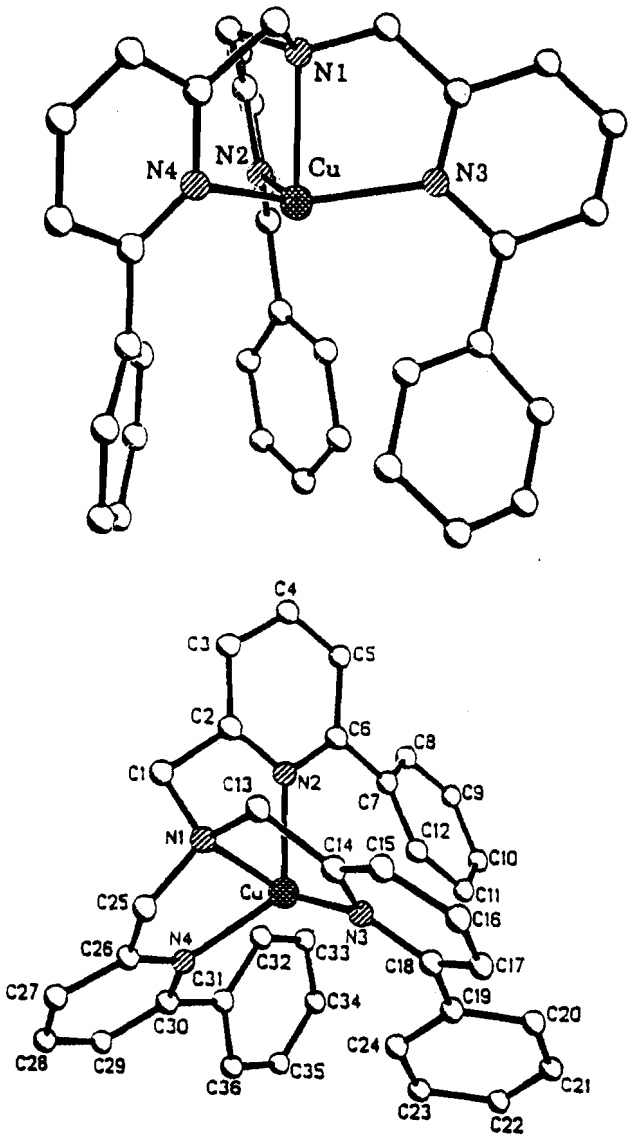

Figure 2. Cationic portion of $[Cu(TPPA)]BPh_4$ (**7**). An AN solvate was present in the crystal lattice of **7** (not shown).

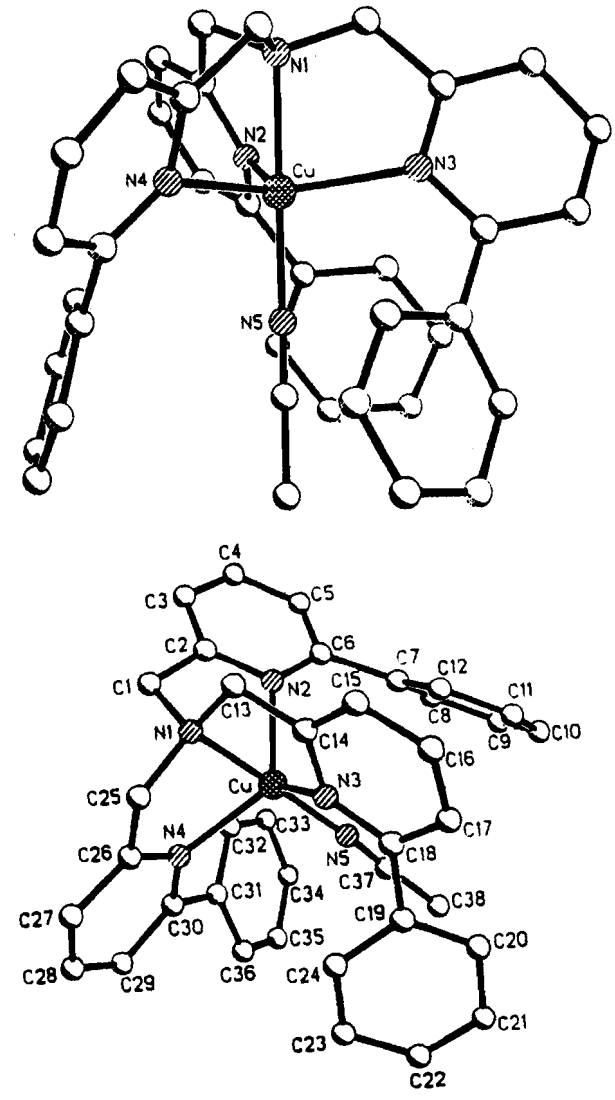

Figure 3. Cationic portion of $[Cu(TPPA)(AN)](ClO_4)_2$ (**8**). The propeller twist is significantly more pronounced in **8** than in **7** in order to create a cavity in which to bind the guest molecule. (Little or no rotation occurs about the pyridyl–phenyl bond.)

phthalimide.[49] Methanolic $NaCNBH_3$ and excess **4** converted **6** to **2** in 67% yield.[42] Green crystals of $[Cu(TPPA)(AN)](ClO_4)_2$ (**8**) were isolated from reaction of $Cu(ClO_4)_2$ with the free ligand in AN/water. The complex $[Cu(TPPA)]BPh_4$ (**7**) was isolated by treating the free ligand with $Cu(NO_3)_2(H_2O)_3$ followed by excess $NaBPh_4$ in acetonitrile/water.[43] Complex **7**, which is unstable in chloroform solution, was isolated as yellow crystals. The X-ray structures of complexes **7** and **8** are shown in Figures 2 and 3.

X-ray Structures. It was possible to obtain structural characterization of both Cu(I) and Cu(II) complexes of **2**. In the structures which were determined, all of the nitrogen atoms of **2** ligate the metal ion despite the presence of the bulky phenyl substituents. In the Cu(II) complex **8**, an additional AN ligand was observed, encased in a cavity defined by the phenyl substituents.

A feature of the structure of **7** is the distortion of the trigonal pyramidal coordination geometry of the Cu(I) ion. Trigonal pyramidal copper(I) geometries are known in proteins[50,51] and model complexes,[10] but the large distortion in the present case is remarkable. The Cu(I) atom lies 0.32 Å above the plane defined by the pyridine nitrogen atoms, away from the fourth ligand. The four Cu–N bond lengths fall in the range 2.08–2.15 Å. It is also of interest to note that the average distance between the copper ion and the three nearest phenyl C-2 atoms is 3.18 Å. Thus, the average distance between the copper ion and the calculated positions of each proton is 2.53 Å. (Shorter Cu–H distances have been reported.)[52] This distance is in the range reported to accompany agostic interactions,[53] but the expected ^1H NMR chemical shifts that generally accompany this phenomenon were not observed.

The copper atom geometry in **8** resembles that in **7** with an additional apical ligand present (AN). The Cu–N(1) bond is longer in **7** than in **8** (2.15 vs 2.00 Å), but all other bonds and angles are very similar, and the distance of the copper atom above the plane containing the pyridine nitrogen atoms is very similar (0.32 vs 0.35 Å). The coordination geometry about the Cu atom in **8** also closely resembles that in the structure of $[Cu(TPA)(AN)](ClO_4)_2$ (**9**)[54,55] and other Cu(TPA) complexes.[9] The average Cu–N(py) bond distance is 2.11 Å in **8** compared

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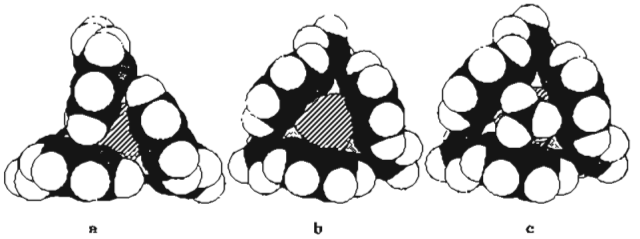

Figure 4. Space-filling models generated from X-ray coordinates: (a) compound **7**; (b) compound **8** with AN guest omitted to emphasize positional change of phenyl substituents compared to **7**; and (c) compound **8**.

Table 1. Summary of Crystal and Refinement Data for $[Cu(TPPA)](BPh_4)$ (**7**) and $[Cu(TPPA)(AN)](ClO_4)_2$ (**8**)

	7	**8**
formula	$C_{62}H_{53}BCuN_5$	$C_{38}H_{33}Cl_2CuN_5O_8$
fw	942.4	822.1
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	14.603(3)	13.458(3)
b, Å	15.137(3)	13.586(3)
c, Å	12.974(3)	11.082(2)
α, deg	91.76(3)	113.00(3)
β, deg	105.87(3)	94.48(3)
γ, deg	117.00(3)	90.53(3)
V, Å^3	2417.4(12)	1857.7(9)
Z	2	2
D(calc), g cm^{-3}	1.295	1.470
μ(MoKα), mm^{-1}	0.499	0.791
temp, K	296	296
cryst size, mm	0.15 × 0.16 × 0.14	0.12 × 0.13 × 0.10
cryst color, habit	yellow, block	green, block
diffractometer	Siemens R3m/V	AFC5S
monochromator	graphite cryst	graphite cryst
radiation	Mo Kα	Mo Kα
wavelength, Å	0.710 73	0.710 73
$2\theta_{max}$, deg	45.0	45.0
no. of rflns collid	6330	6536
no. indept rflns	2917 ($F > 6.0\sigma(F)$)	3575 ($F > 6.0\sigma(F)$)
R	0.0659	0.0733
R_w	0.0707	0.0857
GOF	2.56	2.28

with 2.06 Å in **9**. This shortening of the equatorial bond lengths is accompanied by slight lengthening of the axial bonds: The Cu−N(1) bond length is 2.00 in **8** vs 2.02 Å in **9**; the Cu−N(nitrile) bond length is 1.94 Å in **8** vs 1.98 Å in **9**.

As might be expected, close contacts are observed between the bound AN and the phenyl substituents in the Cu(II) complex. The nitrogen atom of the nitrile (N-5) is within 3.10 Å of 5 carbon atoms of the ligand (e.g., C-19, C-24). The sum of the van der Waals radii for the nitrile N and a phenyl C is 3.47 Å. The carbon atom of the nitrile is an average of 3.37 Å from two of the phenyl C-1 atoms and 3.45 Å from 4 other phenyl atoms (e.g., C-19, C-24). The sum of the van der Waals radii for a nitrile C and a phenyl C is 3.57 Å. The observed distances are close to those found in stacked aromatic rings engaged in favorable π-π interactions.[56,57] Shorter nonbonded distances have been observed in copper(II)-coordinated nitriles.[58−60] Crystal data, coordinates, and bond distances and angles are listed in Tables 1−4.

Table 2. Positional Parameters and U(eq) Values for $[Cu(TPPA)(AN)](ClO_4)_2$ (**8**)

	x	y	z	U(eq), Å^2
Cu	2611(1)	1896(1)	4966(1)	46(1)
N(1)	2401(5)	1267(5)	3004(6)	56(3)
N(2)	3764(4)	2710(5)	4528(6)	45(3)
N(3)	1131(4)	2320(4)	4706(6)	50(3)
N(4)	2846(5)	270(5)	4635(6)	51(3)
N(5)	2785(5)	2490(5)	6869(6)	48(3)
C(1)	3403(6)	1146(5)	2522(8)	61(2)
C(2)	4076(6)	2098(6)	3358(8)	48(2)
C(3)	4975(6)	2309(7)	2961(8)	57(2)
C(4)	5567(7)	3156(7)	3807(8)	62(2)
C(5)	5252(6)	3802(7)	4974(8)	55(2)
C(6)	4324(6)	3585(6)	5318(7)	47(2)
C(7)	3898(6)	4321(6)	6507(7)	47(2)
C(8)	4483(7)	4760(7)	7711(8)	66(3)
C(9)	4061(8)	5440(8)	8826(10)	80(3)
C(10)	3095(8)	5709(8)	8750(10)	83(3)
C(11)	2516(7)	5321(7)	7576(9)	75(3)
C(12)	2911(6)	4616(7)	6453(8)	59(2)
C(13)	1784(7)	2012(7)	2633(9)	71(3)
C(14)	1040(7)	2479(7)	3591(9)	61(2)
C(15)	277(8)	3099(8)	3355(11)	88(3)
C(16)	−344(9)	3550(9)	4324(11)	99(4)
C(17)	−271(8)	3359(8)	5445(10)	84(3)
C(18)	465(7)	2692(7)	5596(8)	59(2)
C(19)	482(6)	2344(7)	6706(8)	58(2)
C(20)	266(7)	3033(8)	7947(10)	80(3)
C(21)	266(8)	2641(9)	8938(11)	92(3)
C(22)	470(8)	1643(9)	8702(11)	91(3)
C(23)	686(7)	930(9)	7490(10)	86(3)
C(24)	681(6)	1301(7)	6482(9)	66(2)
C(25)	1870(6)	212(7)	2674(8)	62(2)
C(26)	2274(6)	−317(7)	3516(8)	55(2)
C(28)	2382(7)	−1816(9)	4077(10)	83(3)
C(27)	2051(7)	−1418(8)	3214(10)	74(3)
C(29)	2973(7)	−1240(8)	5204(10)	77(3)
C(30)	3239(6)	−165(7)	5448(8)	58(2)
C(31)	3955(6)	458(7)	6552(8)	56(2)
C(32)	4667(6)	1156(7)	6408(8)	60(2)
C(33)	5351(7)	1739(8)	7447(10)	79(3)
C(34)	5341(9)	1592(9)	8614(11)	96(3)
C(35)	4671(8)	926(9)	8761(12)	100(4)
C(36)	3963(8)	356(8)	7748(10)	84(3)
C(37)	2857(6)	2778(7)	7958(9)	53(2)
C(38)	2961(7)	3163(8)	9398(9)	87(3)

Figure 4a shows that in the copper (I) complex **7**, two phenyl rings stack in a "T" configuration as observed in solid benzene and protein aromatic side chains.[56] The space-filling models indicate that the copper (I) is completely encapsulated by the TPPA ligand. In **8**, the ligand contains a cavity in which an AN solvent molecule is bound (Figure 4c). To create the cavity, the ligand undergoes a helical 'twist." The average angle between the best axis of the 6-phenylpyridine "arms" and the Cu−N1 bond in **7** is 14.8°; in **8** it is 36.6°. These angles are achieved solely by rotation about the 2-pyridyl−CH_2 bond. There is little change in the dihedral angles defined by the planes of the pyridines and phenyls in the two complexes (average 40 vs 38°). Thus, the conformational change in the ligand that would be required to create the cavity for the AN in **8** resembles the motion of a flower undergoing anthesis.

Electrochemistry. Our study originated with the serendipitous observation that copper(II) complexes of **2** were easily reduced during electrospray ionization mass spectral analysis, which seemed remarkable since the positive ion mode of electrospray ionization involves electrochemically oxidizing

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Table 3. Positional Parameters and U(eq) Values for [Cu(TPPA)]BPh_4 (**7**)

	x	y	z	U(eq), Å^2
Cu	3673(1)	4620(1)	2089(1)	39(1)
N(1)	3277(6)	3056(6)	1914(6)	40(4)
N(2)	2313(6)	4047(5)	628(6)	36(4)
N(3)	3196(6)	4269(6)	3496(6)	39(4)
N(4)	5153(6)	4798(5)	2008(5)	32(4)
C(1)	2823(8)	2710(8)	729(8)	46(3)
C(2)	2018(8)	3072(7)	255(8)	37(2)
C(3)	1026(8)	2430(8)	−527(8)	47(3)
C(4)	323(9)	2793(8)	−935(8)	57(3)
C(5)	619(9)	3770(8)	−593(9)	56(3)
C(6)	1623(8)	4402(7)	177(8)	38(2)
C(7)	1963(8)	5474(7)	531(8)	38(2)
C(8)	1635(8)	6010(7)	−204(8)	40(3)
C(9)	1922(9)	6999(8)	118(9)	53(3)
C(10)	2554(9)	7488(9)	1150(9)	60(3)
C(11)	2894(9)	6990(8)	1913(9)	58(3)
C(12)	2587(8)	5969(7)	1586(8)	42(3)
C(13)	2500(8)	2582(8)	2493(8)	53(3)
C(14)	2697(8)	3263(8)	3465(8)	48(3)
C(15)	2270(9)	2836(9)	4298(9)	65(3)
C(16)	2363(10)	3449(10)	5109(11)	77(4)
C(17)	2869(9)	4445(9)	5178(10)	67(3)
C(18)	3315(8)	4878(8)	4367(9)	49(3)
C(19)	3927(8)	5975(8)	4453(8)	47(3)
C(20)	3621(11)	6607(10)	4957(10)	76(4)
C(21)	4252(12)	7631(10)	5113(11)	86(4)
C(22)	5111(12)	8046(11)	4852(11)	86(4)
C(23)	5456(11)	7490(10)	4319(10)	83(4)
C(24)	4848(9)	6438(8)	4153(8)	53(3)
C(25)	4311(8)	3078(8)	2409(9)	53(3)
C(26)	5216(8)	3943(7)	2168(8)	39(2)
C(27)	6121(8)	3862(8)	2118(8)	48(3)
C(28)	6948(9)	4638(8)	1946(8)	54(3)
C(29)	6905(8)	5521(8)	1776(8)	50(3)
C(30)	5985(8)	5579(7)	1817(7)	35(2)
C(31)	5889(8)	6482(7)	1614(8)	39(2)
C(32)	4942(8)	6452(8)	975(8)	45(3)
C(33)	4871(9)	7312(8)	741(9)	54(3)
C(34)	5771(9)	8231(9)	1174(9)	60(3)
C(35)	6723(10)	8299(9)	1799(9)	67(3)
C(36)	6801(9)	7427(8)	2025(9)	57(3)

Table 4. Bond Distances (Å) and Angles (deg) for **7** and **8** and a Comparison with Those for **9**

	7	**8**	**9**[55]
	Bond Distances		
Cu−N(1)	2.154(9)	1.996(9)	2.109
Cu−N(2)	2.137(6)	2.092(7)	2.056
Cu−N(3)	2.126(9)	2.108(6)	2.08
Cu−N(4)	2.085(9)	2.124(7)	2.035
Cu−N(5)		1.935(6)	1.977
	Bond Angles		
N1−Cu−N2	81.2(3)	80.1(3)	82.6
N1−Cu−N3	80.8(3)	80.0(3)	81.3
N1−Cu−N4	81.8(3)	81.3(3)	82.4
N2−Cu−N3	112.2(3)	118.5(3)	114
N2−Cu−N4	119.0(3)	116.0(2)	120
N3−Cu−N4	122.0(3)	117.4(2)	120.4
N1−Cu−N5		178.7(3)	178
N2−Cu−N5		101.2(3)	97.7
N3−Cu−N5		99.1(3)	96.9
N4−Cu−N5		98.3(3)	99

conditions. However, others have also reported that coordination complexes can be reduced during mass spectral analysis under these conditions.[61,62]

Redox potentials of copper(II) complexes of **1** have been reported to be quite negative.[9] However, several studies of related copper complexes have been reported in which nonpolar groups located proximal to the metal ion resulted in substantially more stable Cu(I) states. The reduction potentials of complexes **8** and **9** were determined by cyclic voltammetry in four solvents and are listed in Table 5. Potential differences from 300 to 470 mV were observed, with smaller differences being observed in AN and DMF than in IBN and DMA. After obtaining this redox data but prior to obtaining crystallographic data, it seemed possible that the positive redox potential of **8** could be entirely attributable to a distortion of the Cu(II) state by the sterically demanding phenyl substituents. Copper(II) complexes of **1** were known to be five-coordinate whereas copper(I) complexes were expected to be four-coordinate as has been observed with related ligands. If the phenyl groups occluded the fifth coordination site, the complex should be easier to reduce. However, as we have discussed, unfavorable steric interactions between the ligand **2** and the AN ligand in **8** are not evident in the observed X-ray crystal structure. Thus, in AN solvent, other factors must account for the more positive redox potential.[23] In the larger solvents, steric hindrance of solvent coordination to Cu(II) ion in **8** is probably still a major factor in determination of the Cu(I)/Cu(II) redox couple.

Table 5. Redox Potentials (mV, vs NHE)[a]

complex	AN	IBN	DMF	DMA
[Cu(TPPA)(AN)](ClO$_4$)$_2$	300	220	120	240
[Cu(TPA)(AN)](ClO$_4$)$_2$	0.00	−260	−230	−230
Δ	300	480	350	470

[a] Abbreviations: AN = acetonitrile, IBN = isobutyronitrile, DMF = dimethylformamide, and DMA = dimethylacetamide.

The complex **8** is more easily reduced in DMF than DMA even though the redox potential of **9** is the same in both solvents. The latter result is expected since the polarity of the two solvents is very similar, as evidenced by nearly identical solvent dielectric constants.[63] The variation of potential in **8** must be attributable to some inner-sphere effects. The larger size of the DMA solvent molecule may account for this difference; a larger coordinating solvent molecule would be more difficult to accommodate in the Cu(II) oxidation state and would therefore be sterically strained, making the complex easier to reduce in the bulkier solvent. A similar correlation of redox potential with solvent molecule size was observed in AN and IBN; however, the large difference in solvent dielectric constants[63] could also explain the observed data. It should also be noted that, since the observed redox processes require changes in both oxidation state and coordination number, the mechanism of the redox change may not be the same in each solvent.

Analysis of the redox behavior of the complexes in AN is complicated by uncertainty regarding the solution structure of the Cu(I) complexes. The redox potential of **9** is more than 200 mV more positive in AN than in the other three solvents studied (Table 5), suggesting that AN plays some unique role in the solution behavior of this complex. Indeed, Karlin has reported a TPA derivative that forms a complex with Cu(I) when crystallized from AN in which an AN has coordinated to the Cu(I) ion, resulting in a significant lengthening of the Cu-N(1) bond.[17] The overall structure of the complex becomes more like a four-coordinate complex where an AN is bonded to the metal ion and the tertiary amine is weakly bonded. In studies of related ligands, Karlin suggests that differences in the UV−vis spectra of Cu(I) complexes in AN vs CH_2Cl_2 may be diagnostic of the coordination of AN to the Cu(I) ion.[16] While UV-vis data are not available for complex **9**, UV−vis spectra of [Cu(TPPA)]PF_6 show the same qualitative behavior as the [Cu(TMQA)]PF_6 (TMQA = tris(2-quinolylmethyl)amine) com-

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plex reported by Karlin:[16] in CH_2Cl_2, the yellow solution of [Cu(TPPA)]PF_6 shows peaks at λ_{max} (nm) = 239 (46 100), 269 (44 200), and 338 (7600), but in acetonitrile, the spectrum has the following absorbances: 214 (52 300), 244 (46 400), and 279 (38 500). The 338 nm peak in CH_2Cl_2 gradually disappeared when AN was added to the solution. Thus it appears that the AN solution structure of [Cu(TPPA)]PF_6 may differ from that observed in the solid state.

Several other factors may influence the redox potential. One possible influence is the electron withdrawing effect of the phenyl substituents on the pyridine rings. Electron withdrawing groups can reduce the σ-donor ability of the ligand, which would increase the redox potential. However, these effects have been examined in bipyridyl ligands, and phenyl groups are known to exert only small inductive effects as substituents.[64] Another explanation which has been put forward to explain similar observations in related ligand systems is the reduction in the local dielectric due to shielding of the copper atom from the polar solvent by the nonpolar phenyl groups.[21,65] A less polar environment near the metal atom would favor lower charge. An analysis of the redox behavior of a series of related Cu/ligand complexes concluded that environmental effects best explain the positive reduction potential of **8** in acetonitrile.[23] The redox behavior in the other solvents, however, is more complex and probably involves a combination of factors including inner-sphere effects.[23] It is also possible that the "T" stacking arrangement of the phenyl groups as observed in **7** contributes to its relative stability.

To summarize, the complexity of the solution coordination chemistry of the complexes frustrates the detailed analysis of the significant difference in redox potential between **8** and **9**. The only certainty is that the difference in potential is larger in solvents of larger molecular size, which suggests that occlusion of the metal ion's solvent coordination site destabilizes the Cu(II) oxidation state, making the complex easier to reduce. This observation is consistent with the classical explanation of the positive redox potential in copper electron transfer proteins.[39] However, many other factors can also be involved in determination of the redox potential, particularly in these small molecules that lack rigid enforcement of the ligand sphere as found in copper proteins.

Reactivity Studies. There has recently been much research effort devoted to studying oxygen binding and activation in inorganic model compounds.[66,67] In particular, copper complexes of **1** and related ligands have provided insight into many features of $Cu-O_2$ binding, including possible structures, spectroscopic behavior, kinetics and thermodynamics of complex formation, and chemical reactivity.[68] In view of the published results, we decided to look for evidence of reaction of Cu(I) complexes with O_2.

The complex [Cu(TPPA)]PF_6 forms a yellow solution in AN that remains yellow even when bubbling O_2 at room temperature for 30 min. The complex [Cu(TPPA)]PF_6 is very stable in CD_3CN as indicated by ^1H NMR, and the UV−vis spectra of solutions of the same complex in AN or CH_2Cl_2 do not change significantly upon saturation of the solution with O_2. The Cu(I) complexes are completely stable to oxidation in the solid state.

The lack of reactivity may be due to steric or electronic effects. The X-ray data indicate that the complex **8** can accommodate an AN molecule in a cavity formed by the phenyl substituents without severe steric distortion. This would suggest that O_2, which is smaller than AN, should be able to fit into a similar cavity. It would thus be expected that the ligand **2** in the Cu(I) complex could twist slightly in order to open a cavity suitable for O_2 to coordinate to the copper ion. However, the phenyl substituents would constrain the O_2 to coordinate in a linear end-on geometry, and would exclude a bent end-on or η^2 side-on geometry as observed in structurally characterized mononuclear copper complexes.[67,69]

The lack of reactivity of the Cu(I) complexes with O_2 may also be related to the very positive oxidation potential (Table 5).[16] The weak driving force for Cu(I) → Cu(II) does not compensate for the unfavorable one-electron reduction of O_2 to O_2^-. Indeed, it has been shown that the driving force toward Cu_2O_2 chemistry derives from the exothermic reaction of $[LCuO_2]^+$ with $[LCu]^+$.[67]

Conclusions

The present study resulted in a unique opportunity to compare the structures of both Cu(I) and Cu(II) complexes of a TPA derivative. Ligand **2** forms a complex with $Cu(ClO_4)_2$ and AN (**8**) in which the 5-coordinate, trigonal bipyramidal coordination geometry of the copper atom is very similar to that in **9**. Close contacts between the phenyl substituents and the AN ligand are in a range consistent with possible $\pi-\pi$ favorable interaction but are not so close as to suggest steric repulsion. The creation of a cavity suitable to accommodate the coordinating AN is accomplished by rotation about the three $N(1)-CH_2$ bonds, resulting in a large propeller-like twist of the ligand. The X-ray crystal structure of Cu(TPPA)BPh_4 (**7**) displays a lesser twist as a result of the absence of the coordinated solvent molecule. In **7**, the copper ion lies significantly below the basal plane in a distorted trigonal pyramidal geometry.

The phenyl substituents in [Cu(TPPA)(AN)]$(ClO_4)_2$ (**8**) strongly stabilize the reduced state of the copper ion compared with [Cu(TPA)(AN)]$(ClO_4)_2$ (**9**). The physical basis of this effect is difficult to determine due to the changes in coordination number between the complexes. In acetonitrile, the situation is especially complicated due to uncertainty of the coordination of the Cu(I) in solution. The redox potential of **9** in AN compared with the other solvents studied is consistent with an anomalous coordination structure in this solvent. The redox potential differences between **8** and **9** are largest in solvents of larger molecular size, consistent with steric interactions between the phenyl substituents destabilizing the Cu(II) form of the redox couple. The positive redox potential probably contributes significantly to the inability of [Cu(TPPA)]PF_6 to react with O_2, although steric constraints imposed by the phenyl substituents may also contribute.

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Supplementary Material Available: Figures showing a cyclic voltammogram of **7** and UV−vis spectra of [Cu(TPPA)]PF_6 and tables of crystallographic data, atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom parameters for **7** and **8** (19 pages). Ordering information is given on any current masthead page.

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