Studies on Aerobic Reactions of Ammonia/3,5-Di-*tert*-butylcatechol Schiff-Base Condensation Products with Copper, Copper(I), and Copper(II). Strong Copper(II)−Radical Ferromagnetic Exchange and Observations on a Unique N−N Coupling Reaction

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Received June 29, 1995⊗

Stoichiometric quantities of 3,5-di-*tert*-butylcatechol and aqueous ammonia react in pyridine solution to form 2-amino-4,6-di-*tert*-butylphenol. Under an atmosphere of dioxygen the aminophenol is oxidized to either the corresponding iminosemiquinone or iminobenzoquinone. In the presence of Cu(II) iminosemiquinone condensation with the aminophenol gives the Cat-N-SQ radical ligand obtained as the $Cu(py)_2(Cat\text{-}N\text{-}SQ)$ complex. Metal and ligand magnetic orbitals are orthogonal and couple ferromagnetically to give a $S = 1$ molecular spin state at temperatures up to 300 K. In nonpolar solvents the complex undergoes ligand oxidation and disproportionation to give $Cu(Cat\text{-}N\text{-}BQ)_2$. Crystallographic characterization on crystals obtained as the *i*-propanol solvate [orthorhombic, $C222_1$, $a = 19.548(3)$ Å, $b = 24.536(5)$ Å, $c = 23.655(5)$ Å, $V = 11346(4)$ Å^3, $Z = 8$, $R = 0.068$] show that the expected Jahn−Teller distortion appears in the *trans* Cu−O lengths of the equatorial plane rather than for the axial Cu−N lengths. Reactions carried out with both Cu(I) and Cu metal require metal oxidation to give the Cu(II) products obtained. With metallic Cu this occurs by a reaction with iminoquinone to give bis(iminosemiquinone)copper(II). Further reaction of this product with aminophenol gives $Cu(py)_2(Cat\text{-}N\text{-}SQ)$ by condensation, and, with O_2, oxidation gives a coordinated azophenolate ligand in Cu(py)(azophenolate) by a unique N−N bond-forming reaction. Cu(py)(azophenolate) has been characterized crystallographically [monoclinic, $P2_1/n$, $a = 10.990(2)$ Å, $b = 10.736(3)$ Å, $c = 26.848(4)$ Å, $\beta = 98.09(1)°$, $V = 3136(1)$ Å^3, $Z = 4$, $R = 0.048$].

Introduction

Copper amine oxidase enzymes utilize a covalently-bound TOPA (trihydroxyphenylalanine) cofactor in the conversion of primary amines to aldehydes.[2] Mechanistic studies indicate that TOPA quinone is the active form of the cofactor.[3] Transamination of the amine is thought to lead to a reduced aminoresorcinol form of the cofactor that is reoxidized aerobically to the active hydantoin, with hydrogen peroxide and ammonia released as coproducts.

$$RCH_2NH_2 + O_2 + H_2O \rightarrow RCHO + NH_3 + H_2O_2 \quad (1)$$

The copper ion appears to be bound to the TOPA cofactor and it may serve as the site of O_2 binding in the reoxidation process.[2,3] Model studies have provided evidence that $Cu(bpy)^{2+}$ and TOPA, together, may be used to catalyze the aerobic deamination of benzylamine.[4] Quinones, and specifically 3,5-di-*tert*-butyl-1,2-benzoquinone, have been used in amine and amino acid deamination reactions, although, the formation of benzoxazole side-products is often a complication.[5] Catechols undergo condensation with ammonia to give 2-aminophenols and bis(1-hydroxyphenyl)amines.[6] Under oxidative conditions 2-aminophenoxyl radicals are formed that lead to cyclization with formation of phenoxazones, phenoxazines, and aminophenoxazinones in reactions that are often highly unselective.[6] 2-Aminophenols, catechols, or 1,2-benzoquinones in the presence of ammonia and copper catalysts are converted to seminitriles of muconic acid by oxidation of iminoquinone intermediates.[7] Selectivity observed in reactions carried out in the presence of copper ion may indicate that the metal is serving as a template, directing the stereochemistry of condensation and oxidation steps. As a consequence, reactions that yield a complicated array of products may be more specific in the presence of a metal ion. Further, in cases where the metal is present in stoichiometric concentrations, products may be obtained in the form of a metal complex. As a specific example, the condensation of ammonia with 3,5-DBCat under aerobic conditions proceeds to form a complicated series of cyclic and acyclic products,[6] but in the presence of metal ion complexes of oxidized forms of bis(1-hydroxyphenyl)amine are obtained in relatively high yield.[8−11] The ligand that appears in these complexes may exist in several charged forms; the two most common forms have been identified as the Cat-N-BQ anion and Cat-N-SQ radical dianion (**I**).[10] With copper as the coordinating

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⊗ Abstract published in *Advance ACS Abstracts*, May 1, 1996.

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S0020-1669(95)00805-6 CCC: $12.00

I

metal the course of the reaction is unusually dependent upon conditions. This may be related to the reduced number of strong coordination sites of Cu^{2+} relative to metal ions with lower d-configurations that appear earlier in the first transition series. As a continuation of our investigations into the coordination chemistry of aminophenols, iminoquinones, and iminosemiquinone radicals we have conducted a study on the oxygenation of 3,5-DBCat in the presence of ammonia and either metallic copper, CuCl, or $CuCl_2$.[12,13]

Experimental Section

Materials. 3,5-Di-*tert*-butylcatechol (3,5-DBCat) was prepared by a published procedure.[14] CuCl, $CuCl_2 \cdot 2H_2O$, and NH_4OH were obtained from Reanal (Budapest, Hungary). Solvents were purified by standard methods, and all reactions were carried out under an atmosphere of dioxygen using standard Schlenk-type glassware.

Reaction of 3,5-DBCat, Metallic Cu, and Ammonia in Pyridine under an Atmosphere of O_2. Cu powder (0.635 g, 10 mmol), 3,5-DBCat (5.35 g, 24 mmol) and 25% NH_4OH (1.9 mL, 25 mmol) were dissolved in 40 mL of pyridine and stirred at room temperature under an atmosphere of O_2. The color of the solution was initially dark green, but it became dark red after approximately 10 min. After approximately 1 h an exothermic reaction took place. The temperature of the mixture increased to 40 °C and a dark colored material deposited. This product was isolated by filtration, dried in vacuum, and extracted with ether. Slow evaporation of the ether filtrate gave thin platelike green crystals of a product subsequently identified as $Cu(py)_2$(Cat-N-SQ) in 36% yield (1.82 g). Mp: 181−184 °C. UV−vis (CH_2Cl_2): λ_{max}/nm (ϵ/M^{-1} cm^{-1}) 235 (26 000), 289 (10 300), 390 (17 500), 525 (2200), 598 (1600), 920 (5400), 1042 (5300). Anal. Calcd for $C_{38}H_{50}N_3O_2Cu$: C, 70.82; H, 7.82; N, 6.53. Found: C, 70.70; H, 8.20; N, 6.54.

Cu(py)(azophenolate). The dark red pyridine filtrate obtained in the procedure above was reduced in volume to give dark red crystals of Cu(py)(azophenolate) in 46% yield (2.23 g). Mp: 184 °C. UV−vis (CH_2Cl_2): λ_{max}/nm (ϵ/M^{-1} cm^{-1}) 214 (9400), 284 (3200), 358 (3100), 388 (3500), 523 (3160), 889 (1300). Anal. Calcd for $C_{33}H_{45}N_3O_2Cu$: C, 68.42; H, 7.83; N, 7.25. Found: C, 69.16; H, 7.07; N, 7.20.

$Cu(Cat\text{-}N\text{-}BQ)_2$. Recrystallization of $Cu(py)_2$(Cat-N-SQ) from dichloromethane solution in air gave dark green crystals of $Cu(Cat\text{-}N\text{-}BQ)_2$. UV−vis and EPR spectra agree with values reported earlier.[9,10b]

Reaction of 3,5-DBCat, CuCl, and Ammonia in Pyridine under an Atmosphere of O_2. CuCl (1.10 g, 11 mmol), 3,5-DBCat (5.35 g, 24 mmol), and 25% NH_4OH (1.9 mL, 25 mmol) were dissolved in 40 mL of pyridine and stirred at room temperature under an atmosphere of O_2 for 8 h. The color of the solution was dark green, and a dark solid separated from solution. The solid was isolated by filtration, and the reaction products were extracted from the residue with ether. Upon cooling, the ether solution gave dark green crystals of $Cu(py)_2$(Cat-N-SQ) and a red filtrate containing a small quantity of Cu(py)(azophenolate). $Cu(py)_2$(Cat-N-SQ) was obtained in this procedure in 72% yield (5.16 g).

Reaction of 3,5-DBCat, $CuCl_2$, and Ammonia in Pyridine under an Atmosphere of O_2. $CuCl_2 \cdot 2H_2O$ (1.89 g, 11 mmol), 3,5-DBCat (5.35 g, 24 mmol), and 25% NH_4OH (1.9 mL, 25 mmol) were dissolved in 40 mL pyridine and stirred at room temperature under an atmosphere of O_2 for 8 h. The color of the solution was dark green, and a dark solid separated from solution. The solid was isolated by filtration, and the reaction products were extracted from the residue with ether. Upon cooling, the ether solution gave dark green crystals of $Cu(py)_2$(Cat-N-SQ) in 82% yield (6.49 g). No Cu(py)(azophenolate) was obtained from this reaction.

Table 1. Crystallographic data for $Cu(Cat\text{-}N\text{-}BQ)_2 \cdot$2-Propanol and Cu(py)(azophenolate)

	$Cu(Cat\text{-}N\text{-}BQ)_2$	Cu(py)(azophenolate)
formula	$C_{59}H_{88}N_2O_5Cu$	$C_{33}H_{36}N_3O_2Cu$
fw	968.9	570.2
color	dark green	dark red
space group	$C222_1$	$P2_1/n$
a, Å	19.548(3)	10.990(2)
b, Å	24.536(5)	10.736(3)
c, Å	23.655(5)	26.848(4)
β, deg	90.0	98.09(1)
Vol, Å^3	11346(4)	3136(1)
Z	8	4
T, °C	24−26	24−26
λ(Mo Kα), Å	0.710 73	0.710 73
D_{calcd}, g cm^{-3}	1.12	1.18
μ, mm^{-1}	0.427	0.727
R, R_w	0.068, 0.070	0.048, 0.065

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

Physical Measurements. Electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. Magnetic measurements were made using a Quantum Design SQUID Magnetometer at a field strength of 5 kG. Infrared spectra were recorded on a Perkin-Elmer 1600 FTIR with samples prepared as KBr pellets.

Crystallographic Structure Determinations. $Cu(py)_2$(Cat-N-SQ) and $Cu(Cat\text{-}N\text{-}BQ)_2$. Crystals of $Cu(py)_2$(Cat-N-SQ) obtained from pyridine solution formed as thin plates that were unsuitable for crystallographic characterization. Recrystallization from dichloromethane/2-propanol solution in air gave small, dark green, prismatic crystals. Recrystallization from toluene solution gave larger parallelopipeds. A crystal obtained from toluene was mounted and aligned on a Siemens P3F diffractometer. Axial photographs indicated tetragonal symmetry and the centered settings of 20 intense reflections gave cell dimensions of $a = 19.425(4)$ Å and $c = 15.172(4)$ Å. These dimensions were close to the cell dimensions found for $Zn(Cat\text{-}N\text{-}BQ)_2$ ($a = 19.476(3)$ Å, $c = 15.135(6)$ Å) and intensity measurements were used to verify that the space group was $I4_122$, the space group of the Zn analog.[15] In this cell, $Z = 4$ and a 222 crystallographic symmetry is imposed on the molecule. With Cu an anticipated Jahn−Teller distortion would be disordered over all four symmetry-related Cu−O bonds. Crystals obtained from the CH_2Cl_2/2-propanol solution were found to form in the acentric orthorhombic space group $C222_1$ in a unit cell of dimensions given in Table 1. Data were collected by $\theta-2\theta$ scans within the angular range 3.0−40° due to the poor diffracting quality of the crystals. A Patterson map was used to determine the position of the Cu atom, and phases derived from the location of the Cu atom gave the positions of other atoms of the molecule. In final stages of refinement atoms associated with an 2-propanol solvate molecule appeared, and were included. Final cycles of refinement converged with discrepancy indices of $R = 0.068$ and $R_w = 0.070$. Selected atomic coordinates are listed in Table 2. Tables containing a full listing of atom positions, anisotropic displacement parameters, and hydrogen atom locations are available as Supporting Information.

Cu(py)(azophenolate). Dark red prismatic crystals of the complex were obtained by slow evaporation of a pyridine solution. Axial photographs indicated monoclinic symmetry and the centered settings of 25 intense reflections with 2θ values between 21 and 34° gave the unit cell dimensions listed in Table 1. Data were collected by $\theta-2\theta$ scans within the angular range 3.0−45°. A Patterson map was used to determine the position of the Cu atom, and phases derived from the location of the Cu atom gave the positions of other atoms of the structure. Final cycles of refinement converged with discrepancy indices of $R = 0.048$ and $R_w = 0.065$. Selected atomic coordinates are listed in Table 3. Tables containing a full listing of atom positions,

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Table 2. Selected Atomic Coordinates (×10^4) for Cu(Cat-N-BQ)$_2$

	x/*a*	*y*/*b*	*z*/*c*
Cu	416(1)	8018(1)	9406(1)
O1	838(4)	8130(4)	10202(4)
O2	−270(5)	8056(4)	8743(4)
O3	1154(5)	8654(4)	9075(4)
O4	42(5)	7173(4)	9562(4)
N1	−291(6)	8464(4)	9751(5)
N2	1133(7)	7581(5)	9050(4)
C1	507(7)	8482(6)	10479(6)
C2	−129(6)	8704(6)	10230(6)
C3	−474(7)	9147(5)	10517(6)
C4	−254(7)	9337(5)	11017(6)
C5	349(7)	9066(6)	11268(6)
C6	715(7)	8653(6)	11029(6)
C7	−840(9)	8233(5)	8900(6)
C8	−904(7)	8467(5)	9450(7)
C9	−1536(8)	8648(5)	9695(6)
C10	−2094(8)	8608(5)	9365(7)
C11	−2030(8)	8400(6)	8810(7)
C12	−1450(8)	8217(5)	8549(6)
C13	1692(8)	8409(6)	8977(6)
C14	1731(9)	7832(6)	8942(7)
C15	2361(8)	7535(6)	8865(5)
C16	2946(7)	7814(6)	8763(6)
C17	2878(10)	8417(7)	8760(6)
C18	2323(9)	8718(7)	8837(7)
C19	351(7)	6851(6)	9230(6)
C20	958(6)	7068(6)	8942(5)
C21	1288(6)	6711(6)	8542(6)
C22	1084(7)	6194(6)	8423(6)
C23	533(8)	6001(5)	8743(6)
C24	148(7)	6303(7)	9110(7)

Table 3. Selected Atomic Coordinates (×10^4) for Cu(py)(azophenolate)

	x/*a*	*y*/*b*	*z*/*c*
Cu	1381(1)	1529(1)	137(1)
O1	1905(4)	674(4)	751(2)
O2	956(4)	2613(4)	−404(2)
N1	−1(5)	2018(5)	459(2)
N2	−908(5)	2709(5)	307(2)
N3	2666(5)	681(5)	−205(2)
C1	37(6)	1513(7)	943(2)
C2	1112(6)	820(6)	1078(3)
C3	1318(6)	308(6)	1572(2)
C4	414(6)	518(6)	1877(2)
C5	−668(6)	1190(6)	1736(3)
C6	−842(6)	1688(6)	1264(2)
C15	−964(6)	3289(6)	−158(2)
C16	−57(6)	3265(6)	−496(2)
C17	−296(6)	3998(6)	−945(2)
C18	−1396(6)	4630(6)	−1044(2)
C19	−2311(6)	4612(6)	−724(3)
C20	−2065(6)	3974(6)	−293(3)

anisotropic displacement parameters, and hydrogen atom locations are available as Supporting Information.

Results

Condensation reactions involving 3,5-DBCat and ammonia have been studied, and the chemistry described in this report may be traced to the formation of 2-amino-4,6-di-*tert*-butylphenol.[8] As studies on amine condensation reactions involving TOPA models have shown, oxidation reactions involving dioxygen lead to new pathways and a variety of products.[16] It has been the hope of this investigation that the presence of copper will add selectivity and direction to the condensation/oxidation chemistry of this system. We will begin with a description of the most well-understood reaction of the series, the reaction involving CuCl$_2$.

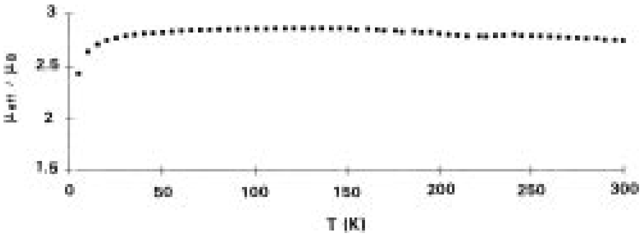
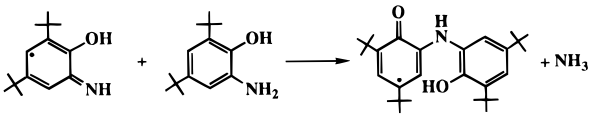


Figure 1. Plot of magnetic moment vs temperature for Cu(py)$_2$(Cat-N-SQ).

Reaction of 3,5-DBCat, CuCl$_2$, and Ammonia in Pyridine under an Atmosphere of O$_2$. Stegmann and Scheffler observed the dimerization of 2-amino-4,6-di-*tert*-butylphenol in reactions that were used to produce complexes of the radical Cat-N-SQ dianion.[8] Condensation was viewed to occur between the *o*-iminosemiquinone, formed by dioxygen oxidation of the aminophenol, and unoxidized aminophenol (eq 2). The product



(2)

of this dimerization is the delocalized Cat-N-SQ radical that readily coordinates with Sn and other main-group and transition metal ions.[8−11] The Cat-N-BQ and Cat-N-SQ charged forms of the ligand (**I**) are found most commonly in complexes, although electrochemical studies have shown that more strongly reduced and oxidized forms of the ligand may exist.[10]

Cu^{II}(py)$_2$(Cat-N-SQ). The chemistry described in eq 2 has been carried out in the presence of Cu^{2+} in pyridine solution. Following the reaction reported by Stegmann and Scheffler with diaryldihalotin substrates, the product obtained in the presence of copper ion is Cu(py)$_2$(Cat-N-SQ). Crystals of the complex form as thin plates that are unsuitable for crystallographic analysis, but the form of the complex is clear from its analytical and spectroscopic properties. Its infrared spectrum is quite similar to spectra of the M(Cat-N-SQ)$_2$ series with additional bands associated with the pyridine ligand.[10,11] Electronic spectra recorded on complexes containing the Cat-N-SQ ligand, and specifically the ligand in this electronic form, show characteristic low-energy absorptions.[10,11] In particular, an intense absorption in the 1000−1100 nm region of the near-IR is commonly observed, and the transition in this region for Cu(py)$_2$(Cat-N-SQ) appears at 1042 nm. The magnetic properties of the complex have been measured as a function of temperature with the result shown in Figure 1. Over the temperature range from 300 to 25 K magnetic moment remains constant at a value of 2.85 μ_B indicating a ferromagnetically spin-aligned $S = 1$ ground state. Below 25 K magnetic moment drops slightly, presumably as an effect of intermolecular coupling. The Cu(py)$_2$(Cat-N-SQ) molecule is, most likely, square pyramidal in structure, with basal and apical pyridine ligands, that are similar to those of the [Cu(py)$_2$(3,5-DBCat)]$_2$ dimer, and with the tridentate Cat-N-SQ ligand occupying the remaining three basal coordination sites.[17] Spins within the molecule lie in orthogonal orbitals, a dσ orbital of the metal and a ligand π-orbital. Parallel spin alignment gives the $S = 1$ spin ground state of the molecule, rather than noninteracting spins that would give a magnetic moment of 2.45 μ_B. Bruni *et al.* have described coupling between orthogonal radical Cat-N-SQ ligands through a diamagnetic metal ion in Ti(Cat-N-SQ)$_2$.[11] Magnetic measurements on this complex showed an increase in magnetic moment,

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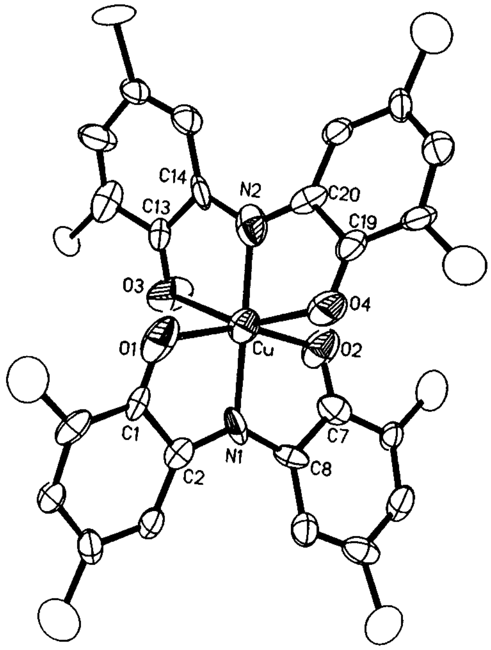

Figure 2. View of Cu(Cat-N-BQ)$_2$ with methyl carbon atoms of *tert*-butyl groups omitted.

from a value of 2.47 μ_B at room temperature where spins are essentially uncorrelated, to a value of 2.77 μ_B at 4 K corresponding to an $S = 1$ state. Ferromagnetic coupling in Cu(py)$_2$(Cat-N-SQ) is considerably stronger in showing no evidence for uncorrelated spins at any temperature, and a J_{Cu-SQ} value exceeding 200 cm^{-1} for $H = -2J_{Cu-SQ}$ ($S_{Cu}\cdot S_{SQ}$).

Cu(Cat-N-BQ)$_2$. Attempted recrystallizations of Cu(py)$_2$(Cat-N-SQ) from nonpolar solvents in air provided large prismatic crystals. Crystallographic characterization indicated that the crystals were, in fact, Cu(Cat-N-BQ)$_2$, a complex originally reported by Girgis and Balch.[9] Characteristic changes in electronic spectrum indicate that Cu(py)$_2$(Cat-N-SQ) undergoes oxidation in air over the period of a few hours in solution, an observation that is in accord with the negative oxidation potential of the Cat-N-SQ ligand in cases where the ligand is not stabilized by π-donation to an acidic metal ion.[10b] Ligand oxidation must be followed by a disproportionation reaction that leads to Cu(Cat-N-BQ)$_2$ and other uncharacterized copper-containing products. Two crystalline forms of Cu(Cat-N-BQ)$_2$ have been obtained, both different from the triclinic crystals obtained with other metal ions.[10,11] Tetragonal crystals were obtained from toluene solution. An earlier structure determination on Zn(Cat-N-BQ)$_2$ was found to be of this crystal system, and the results of low-angle intensity measurements indicated that the space group and unit cell dimensions were similar for Cu(Cat-N-BQ)$_2$.[15] The molecule resides about a site of 222 crystallographically imposed symmetry, with an independent half of one ligand. Consequently, all four Cu−O lengths are required to be the same and both Cu−N lengths are the same. Crystals obtained from a CH$_2$Cl$_2$/2-propanol solution were found to form in the orthorhombic crystal system in a unit cell that contained a molecule of 2-propanol as a solvent molecule of crystallization. In this case there is no symmetry imposed on the molecule. A view of the complex molecule is shown in Figure 2; bond lengths and angles are listed in Table 4. The molecule has approximate 222 symmetry as required by the tetragonal space group, but with significant differences in the Cu−O bond lengths that would be averaged in the tetragonal unit cell. As a complex of d^9 Cu(II) a Jahn−Teller distortion may be expected that might, reasonably, appear as an axial elongation of Cu−N bonds. However, Cu(II) possesses a strong affinity for imine nitrogen donors, and distortion of the octahedron upon axial elongation would be severe. As a consequence, the Cu−N lengths of 1.950(11) Å are relatively short, and the distortion appears as an axial elongation of two *trans* Cu−O bonds. Lengths to oxygen atoms O1 and O2 average to 2.070(9) Å, while lengths to oxygen atoms O3 and O4 of the second ligand average to 2.247(10) Å. Otherwise, features of the Cat-N-BQ ligands are similar to the ligands of Ni(Cat-N-BQ)$_2$ and Zn(Cat-N-BQ)$_2$ with C−O lengths that average to 1.254(18) Å and C−N lengths of 1.347(18) Å. These values compare with C−O and C−N lengths of 1.264(5) and 1.344(5) Å for the Ni analog,[10b] and 1.264(5) and 1.331(3) Å for Zn(Cat-N-BQ)$_2$.[15] Tetragonal crystals of Cu(Cat-N-BQ)$_2$ apparently have the distortion in Cu−O lengths averaged over the four equivalent sites either by static disorder or a dynamic process. Such behavior is not uncommon for octahedral complexes of Cu(II).[18]

Table 4. Selected Bond Lengths and Angles for Cu(Cat-N-BQ)$_2$

	Bond Lengths (Å)		
Cu−O1	2.073(9)	Cu−O2	2.066(9)
Cu−O3	2.264(10)	Cu−O4	2.230(10)
Cu−N1	1.943(11)	Cu−N2	1.956(12)
O1−C1	1.262(17)	O2−C7	1.253(19)
N1−C2	1.317(18)	N1−C8	1.394(19)
C1−C2	1.479(18)	C7−C8	1.429(22)
O3−C13	1.233(19)	O4−C19	1.268(17)
N2−C14	1.346(21)	N2−C20	1.329(19)
C13−C14	1.419(21)	C19−C20	1.468(19)
	Angles (deg)		
O1−Cu−O2	160.3(4)	O3−Cu−O4	155.1(4)
N1−Cu−N2	178.9(5)		

Reaction of 3,5-DBCat, Metallic Cu, and Ammonia in Pyridine under an Atmosphere of O$_2$. The combination of 3,5-DBCat, ammonia and pyridine, alone, are not sufficient to react with Cu metal, but in the presence of dioxygen two complex products are formed in nearly equal quantities in high yield. Under the conditions used for the reaction Cu(py)$_2$(Cat-N-SQ) separates from solution leaving a second, dark red product in the pyridine filtrate.

Cu(py)(azophenolate). Evaporation of the red solution gave crystals of the second product. Crystallographic characterization indicated that the complex was a planar molecule containing a tridentate azophenolate ligand formed by the oxidative dimerization of two iminoquinone ligands. A view of Cu(py)(azophenolate) is shown in Figure 3; bond lengths and angles are contained in Table 5. The azophenolate ligand forms both five- and six-membered chelate rings with the metal. Features of the quinone fragment associated with the five-membered ring are relatively normal with a slightly contracted C1−C2 length, but, otherwise, aromatic C−C ring lengths and single-bond C−O and C−N lengths. The fragment containing O2 shows evidence of conjugation and charge delocalization through to N1. The C16−O2 length and the ring C17−C18 and C19−C20 bonds are all slightly contracted, and the N1−N2 length is longer than a localized double bond value. The toluene solution EPR spectrum is quite typical of planar Cu(II) in consisting of a four-line pattern with $\langle g \rangle = 2.006$ and $A(^{65,63}\mathrm{Cu}) = 91.7$ G. A five-line coupling pattern to the two nitrogen donors appears on the high-field component of the spectrum. In toluene glass at 77 K the spectrum splits to give $g_\perp = 2.05$ and $g_\parallel = 2.19$, with $A_\parallel(^{65,63}\mathrm{Cu}) = 198$ G and $A_\perp(^{14}\mathrm{N}) = 17.9$ G.

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(18) Bernhardt, P. V.; Bramley, R.; Engelhardt, L. M.; Harrowfield, J. M.; Hockless, D. C. R.; Korybut-Daszkiewicz, B. R.; Krausz, E. R.; Morgan, T.; Sargeson, A. M.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **1995**, *34*, 3589.

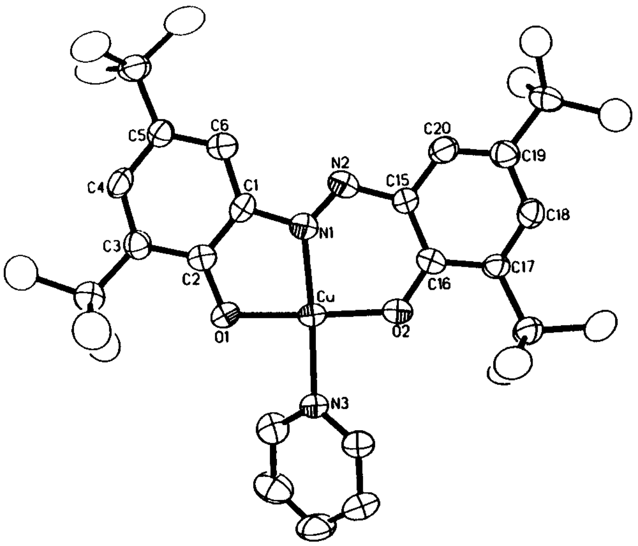


Figure 3. View of Cu(py)(azophenolate).

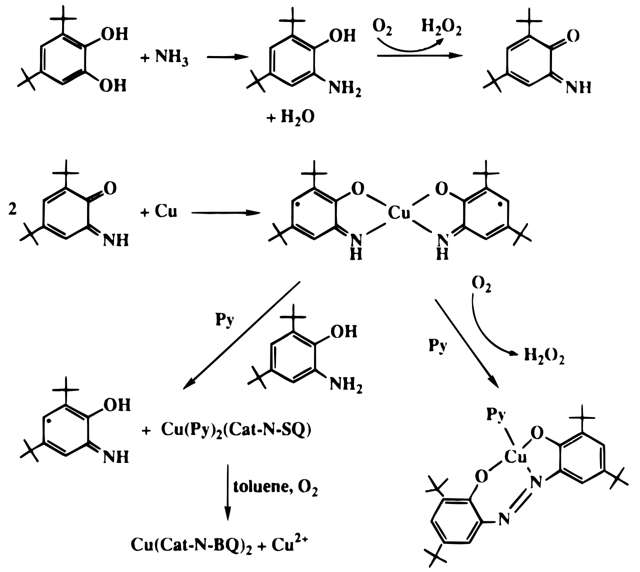
Table 5. Selected Bond Lengths and Angles for Cu(py)(azophenolate)

	Bond Lengths (Å)$^-$		
Cu−O1	1.905(4)	Cu−O2	1.867(4)
Cu−N1	1.923(6)	Cu−N3	2.007(6)
O1−C2	1.331(9)	O2−C16	1.309(8)
N1−N2	1.263(8)	N1−C1	1.405(8)
N2−C15	1.390(9)	C1−C2	1.400(9)
C1−C6	1.394(10)	C2−C3	1.423(9)
C3−C4	1.393(10)	C4−C5	1.397(9)
C5−C6	1.363(9)	C15−C16	1.440(10)
C15−C20	1.418(9)	C16−C17	1.432(9)
C17−C18	1.379(9)	C18−C19	1.412(10)
C19−C20	1.339(9)		
	Angles (deg)		
O1−Cu−O2	170.2(2)	O1−Cu−N1	84.5(2)
O2−Cu−N1	93.0(2)	N1−Cu−N3	168.5(2)
C1−N1−N2	116.4(6)	C15−N2−N1	119.1(6)

Formation of Cu(py)$_2$(Cat-N-SQ) and Cu(py)(azophenolate). The key step in the reaction with metallic Cu is the initial oxidation of the metal. Schiff-base condensation occurs rapidly between ammonia and 3,5-DBCat to give the aminocatechol, and under the basic conditions of the reaction, the aminocatechol is then oxidized in air to ultimately give the iminobenzoquinone (Scheme 1). The iminobenzoquinone PhenoxBQ has been observed to easily react with metallic copper giving Cu^{II}(PhenoxSQ)$_2$.[12] By analogy, we propose that copper oxidation occurs by a reaction with the iminobenzoquinone formed by dioxygen oxidation of the parent aminophenol to give the planar bis(iminosemiquinonato)copper(II) complex. In this way, metallic Cu is stoichiometrically oxidized to Cu(II). The iminosemiquinone ligands of the product may react in one pathway with an unoxidized aminophenolate to give Cu(py)$_2$(Cat-N-SQ). Air oxidation of bis(iminosemiquinone)copper(II), with ligand coupling may be responsible for formation of the azophenolate ligand of Cu(py)(azophenolate). It is likely that the bis(iminosemiquinonato)copper(II) species forms as both *cis* and *trans* isomers, and this structural difference may be related to the differences in pathway leading to the two products.

Reaction of 3,5-DBCat, CuCl, and Ammonia in Pyridine under an Atmosphere of O$_2$. The related 3,5-DBCat/NH$_3$/O$_2$ reaction carried out in the presence of Cu(I) contains elements of both previous reactions in giving Cu(py)$_2$(Cat-N-SQ) as the major product with a small quantity of Cu(py)(azophenolate). Prior studies have shown that the iminobenzoquinone formed by the dioxygen oxidation of aminophenol is incapable of oxidizing Cu(I).[13] As in the previous reaction, a metal oxidation step is necessary for the formation of both products. The major product, Cu^{II}(py)$_2$(Cat-N-SQ), may form *via* a mechanism that is similar to the reaction described above for Cu(II), with initial formation of [Cu^{I}(py)(Cat-N-SQ)]$^-$. Dioxygen oxidation would give the Cu(II) product. Cu(py)(azophenolate) is observed as a minor product of the reaction. It is likely formed by oxidation of bis(iminosemiquinonato)copper(II), as in Scheme 1, which, in turn, is formed from Cu(0) that results from some small disproportionation of Cu(I) in the reaction.[19]

Scheme 1



Discussion

The feature that is common to all three synthetic procedures beginning with Cu(II), Cu(I), and Cu(0) is the formation of Cu(py)$_2$(Cat-N-SQ) as a major product. It is easy to understand the chemical steps leading to this product in the context of the chemistry defined much earlier by Stegmann and Scheffler.[8] With Cu(I) and Cu(0) metal oxidation steps are necessary, but viable reactions with dioxygen can be envisioned as leading to the Cu(II) products. A particularly noteworthy feature of this complex is the strong ferromagnetic coupling between the metal and the radical ligand. As a molecule that is in the $S = 1$ spin state at all temperatures, it contains an exceptionally strong Cu(II)−radical coupling interaction, and the Cu^{II}(Cat-N-SQ) subunit may be useful in the synthesis of extended polymers that will exhibit cooperative ferromagnetic properties.

Structural features of Cu(Cat-N-BQ)$_2$ showed an unexpected Jahn−Teller distortion, at *trans* equatorial oxygen-donor sites rather than along the tetragonal axis of the molecule. This distortion appears to be averaged over both ligands of Cu(Cat-N-BQ)$_2$ in the tetragonal crystal system.

Considerable interest has been directed to investigations on catalytic deamination reactions that might parallel the chemistry associated with the quinone-containing copper amine oxidase enzymes.[3,4,16] These reactions have been investigated in both the presence and absence of Cu(II), and the catalytic role of the metal in these reactions is to provide the capability for autoxidative aerobic recycling of the reduced catalyst. Recent work by Sayre has indicated that the mode of Cu−TOPA coordination is important in defining the role of the metal, as either a catalyst or inhibitor.[16] Many of the condensation steps

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(19) Tezuka, Y.; Miya, M.; Hashimoto, A.; Imai, K. *J. Chem. Soc., Chem. Commun.* **1987**, 1642.

associated with this chemistry parallel reactions that occur with the DBCat/NH_3/O_2 system, and the presence of copper, as either oxidized Cu(II) or reduced Cu(I) or Cu(0), may aid in the isolation and characterization of products that include otherwise unstable radical intermediates. Formation of the azophenolate species bound to Cu in Cu(py)(azophenolate) was unexpected and it apparently results from oxidative dimerization of iminosemiquinone ligands at the metal ion. Products containing N−N bonds have not been observed previously in this chemistry. Reactions that form azoaryl functionalities directly from amines are unusual, and details of the reaction are under further investigation.

Acknowledgment. We would like to thank Brenda Conklin for help with magnetic measurements. Support for research carried out at the University of Colorado was provided by the National Science Foundation (Grant CHE-93636). Research at the University of Veszprem as supported by the Hungarian Research Fund (Grant OTKA-2326). CGP and GS would like to thank the US−Hungarian Joint Fund for collaborative research support through Grant 098/91.

Supporting Information Available: Tables giving crystal data and details of the structure determination, atomic coordinates, anisotropic thermal parameters, hydrogen atom locations, and bond lengths and angles for Cu(Cat-N-BQ)$_2$ and Cu(py)(azophenolate) (26 pages). Ordering information is given on any current masthead page.

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