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Valence Tautomerism and Metal-Mediated Catechol Oxidation for Complexes of Copper Prepared with 9,10-Phenanthrenequinone

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Bis(pyridine)(9,10-phenanthrenequinone)(9,10-phenanthrenediolato)copper(II), $Cu(py)_2(PhenCat)(PhenBQ)$, has been prepared by treating copper metal with 9,10-phenanthrenequinone in pyridine solution. In dilute solution, both $Cu(py)_2(PhenCat)(PhenBQ)$ and the related complex Cu(tmeda)(PhenCat)(PhenBQ) lose PhenBQ to form $Cu^{II}L_2(PhenCat)$, where L_2= tmeda, 2 py. EPR spectra recorded at temperatures between 300 and 77 K reveal the presence of species with radical and metal localized spins together at equilibrium. Equilibria between $Cu^{II}L_2(PhenCat)$ and $Cu^{I}L_2(PhenSQ)$ redox isomers are solvent dependent, with a shift to higher temperature for polar solvents. Both complexes are oxygen sensitive, reacting with dioxygen to give complexes of diphenic acid. Structural characterization on products obtained with tmeda show that dioxygen insertion across the C−C bond within the chelate ring leads to dimeric products with adjacent Cu(II) ions bridged by diphenate ligands. The addition of O_2 to Cu(tmeda)(PhenCat) in acetonitrile solution at 0 °C appears to form a peroxo complex, tentatively identified as $Cu(tmeda)(O_2)(PhenQ)$ on the basis of iodometric titration, as the precursor to the diphenate complex.

Introduction

Significant research directions that have developed around studies on the coordination chemistry of catecholate (Cat) and semiquinonate (SQ) ligands include the aerobic oxidation of coordinated catecholate ligands and the facile metal−quinone electron-transfer associated with valence tautomerism.

Catecholate [M^{II}(Cat)] and semiquinonate [M^{I}(SQ)] redox isomers differing in charge distribution have been observed together in solution and the solid state under equilibrium conditions.[1] Compounds that exhibit valence tautomerism have metal and quinone electronic levels that are close in energy as a result of coligand-donation and quinone-substituent effects. Charge localization is necessary to provide the thermodynamic changes that define the temperature range ($T_{1/2}$) for equilibrium measurements. Systems that have been studied most intensively have changes in the occupancy of dσ orbitals directed at ligand donor sites. Occupancy of this antibonding orbital destabilizes the M−L bonds of a rigid, tightly bound [M^{II}(Cat)] redox isomer, leading to the formation of a loosely bound, fluxional [M^{I}(SQ)] redox isomer. The shift in charge distribution results in a large positive entropy change that offsets the unfavorable change in enthalpy, which results from weakened bonds. Complexes of cobalt, with shifts in charge distribution occurring between rigid low-spin Co(III) and flexible high-spin Co(II), have been studied in greatest detail.[1] Manganese complexes have also been shown to undergo reversible shifts in charge distribution.[1a] The transition from the tightly bound d^3 Mn(IV) form of $Mn^{IV}(Cat)_2$ to the high-spin d^5 Mn(II) ion of $Mn^{II}(SQ)_2$ occurs through the Jahn−Teller distorted d^4 Mn(III) redox isomer, Mn^{III}(SQ)(Cat). Recently, similar shifts in charge distribution have been described for the Cu^{II}(Cat) and Cu^{I}(SQ) redox isomers of copper. [1a]

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Thermodynamic effects that make equilibria of this type favorable for copper are less clear with the change in metal ion configuration from d^9 to d^{10}, and we have sought to find well-defined quinone complexes of copper for study.

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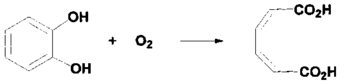
The aerobic oxidation of catechol occurs in biological systems,[2] and it has been of interest in commercial syntheses.[3] The most widely studied substrate is 3,5-di-*tert*-butylcatechol ($H_2$3,5-DBCat), and oxidations are generally carried out in the presence of a Lewis acid metal ion.[4] In a few cases of specific interest, the metal is actively involved with dioxygen binding and catechol substrate oxidation to a dicarboxylate (1). Questions regarding the mechanism of dioxygen activation, the form of peroxo intermediates, and stereoselectivity, intra- vs extradiol ring cleavage, remain as subjects of investigation.



Complexes of copper have appeared prominently in these investigations. A report by Brown in 1977 on (bpy)Cu^{II}(3,5-DBCat) was one of the earliest reports on the stoichiometric dioxygenation of a coordinated catecholate ligand.[5] Que and Lipscomb have studied the bioinorganic chemistry of the extradiol and intradiol catechol dioxygenase enzymes.[2a] The extradiol dioxygenase enzymes contain a singly protonated catechol substrate ligand chelated to Fe(II) (or Mn(II)) at the active site. Dioxygen is thought to bind initially at a vacant coordination site of the metal ion in the oxidation process. The intradiol dioxygenase enzymes have Fe(III) at the active site. Dioxygen addition occurs at a chelated catecholate ligand as the nucleophilic center of the complex. Que has provided a number of relevant iron(III) complexes of 3,5-DBCat that undergo oxidative ring cleavage upon exposure to air. Potentially relevant to the mechanism of dioxygen activation, Bianchini[6] and, recently Bhattacharya,[7] have isolated peroxosemiquinone complexes as products of dioxygen addition to a chelated phenanthrenediolate ligand. It is of interest, however, that these species fail in further reactions that lead to ring-opened products.

In this report we describe observations on complexes of copper prepared from 9,10-phenanthrenequinone. The results of this study touch on both the effects leading to valence tautomerism in complexes of copper and the aerobic oxidation of a chelated quinone (either SQ or Cat) ligand.

Experimental Section

Materials. Reagent grade chemicals were used in all experiments, and solvents were purified by standard procedures. Reactions were carried out under an atmosphere of dry argon, unless otherwise indicated. Samples of Cu(tmeda)(PhenCat)(PhenBQ) were prepared using procedures described previously.[8]

Preparation of Cu(py)$_2$(PhenCat)(PhenBQ). A pyridine solution (50 mL) containing 9,10-phenanthrenequinone (2.1 g, 10 mmol) and copper wire (5 g) was heated at reflux for 24 h. The dark green solution was cooled to room temperature and filtered. The filtrate was condensed with a flow of dry Ar. Red pleochroic crystals were obtained (1.53 g, 2.4 mmol) that, when ground, gave a green powder. Anal. Calcd for $C_{38}H_{26}N_2O_4Cu$: C, 71.5; H, 4.1; N, 4.4. Found: C, 72.1; H, 4.2; N, 4.1. IR (cm^{-1}, KBr): 1676m, 1623m, 1597m, 1580s, 1564m, 1536m, 1486m, 1448m, 1393s, 1340m, 1323m, 1285m, 1251s, 1148m, 1090m, 1058m, 1026s, 800m, 755m, 700m, 551w, 436w.

Preparation of Cu(tmeda)(PhenCat). An acetonitrile (50 mL) solution containing 9,10-phenanthrenequinone (2.1 g, 10 mmol), tmeda (1.65 mL, 11 mmol), and metallic copper (5.0 g, 78.7 mmol) was heated at reflux for 20 h. Excess metallic copper was separated from the solution by filtration. The volume of the solution was reduced to approximately 20 mL, and it was cooled to 0 °C. Off-white crystals of Cu(tmeda)(PhenCat) formed as thin, flat plates in 92% yield (3.5 g). Anal. Calcd for $C_{20}H_{24}N_2O_2Cu$: C, 61.9; H, 6.2; N, 7.2. Found: C, 62.0; H, 6.3; N, 7.1. UV−vis: 270 nm (7.8×10^3 M^{-1} cm^{-1}), 315 (2.9×10^3), 815 (40). IR (cm^{-1}, KBr): 1689w, 1601m, 1577s, 1491w, 1481s, 1379s, 1349s, 1290m, 1233w, 1121w, 1061s, 1027s, 957w, 814m, 797m, 777s, 727m, 697w, 590m, 563w, 506w.

Preparation of [Cu(tmeda)(diphenate)]$_2$. Cu(tmeda)(PhenCat) (0.53 g, 1.36 mmol) was stirred in acetonitrile (10 mL) at room temperature under an atmosphere of dioxygen for 2.5 h. O_2 uptake was monitored and found to be 31 mL (∼1.24 mmol). Upon cooling, pale blue crystals of the compound, subsequently identified as [Cu(tmeda)(diphenate)]$_2$·0.5CH_3CN, separated from the solution. Recrystallization of [Cu(tmeda)(diphenate)]$_2$ from acetonitrile containing trace quantities of water led to [Cu(tmeda)(H_2O)(diphenate)]$_2$. Anal. Calcd for $C_{20}H_{26}N_2O_5Cu$: C, 54.8; H, 6.0; N, 6.4; Cu, 14.5. Found: C, 55.3; H, 6.0; N, 6.9; Cu, 14.7. UV−vis: 272 nm (5.1×10^3 M^{-1} cm^{-1}), 654 (53). IR (cm^{-1}, KBr): 1609s, 1588s, 1557s, 1467s, 1447s, 1407vs, 1283w, 1042w, 1022w, 1003w, 954m, 853m, 810m, 763s, 719m, 683w, 665w.

Oxygenation of Cu(tmeda)(PhenCat) in Acetonitrile at 0 °C. Cu(tmeda)(PhenCat) (1.1 g, 2.8 mmol) suspended in acetonitrile (20 mL) was placed under an atmosphere of O_2 for 4 h at 0 °C. The Cu(tmeda)(PhenCat) dissolved slowly during O_2 uptake (81 mL, 3.53 mmol) to give a homogeneous blue solution. On standing in the refrigerator, green crystals of a species identified as Cu(tmeda)(PhenCat)(O_2) separated from the solution. The product was isolated by filtration and dried under vacuum (yield 1.14 g, 97%). Anal. Calcd for $C_{20}H_{24}N_2O_4Cu$: C, 57.2; H, 5.7; N, 6.7; Cu, 15.1. Found: C, 58.9; H, 5.1; N, 6.7; Cu, 15.4. IR (cm^{-1}, KBr): 1678s, 1593s, 1460sh, 1449s, 1372m, 1275sh, 1251sh, 1208s, 1144m, 1089m, 1024s, 990s, 962m, 944m, 819sh, 803m, 757sh, 749s, 724m. Magnetic moment: $\mu_{eff} =$ 2.03 μ_B/Cu.

Peroxide Content of Cu(tmeda)(PhenCat)(O_2). Cu(tmeda)(PhenCat)(O_2) (1.3 g, 3 mmol) was dissolved in dichloromethane (20 mL) and acidified with 20% sulfuric acid (20 mL). The mixture was stirred for 20 min, and the solvent layers were separated. The aqueous layer was extracted again with dichloromethane (20 mL), and the hydrogen peroxide content of this layer was determined by iodometry.[9] Iodometric titration gave a peroxide content of 0.0023 mmol/mg (96.5%/mol) for the peroxo complex.

Acid Hydrolysis of Cu(tmeda)(PhenCat)(O_2). Cu(tmeda)(PhenCat)(O_2) (5 g, 11.9 mmol) was treated with 5% sulfuric acid (100 mL) and extracted with dichloromethane (3 × 20 mL). The organic layer was dried with Mg(SO_4), and the PhenBQ content was determined spectrophotometrically ($\lambda_{max} = 417$ nm (1.74×10^3 M^{-1} cm^{-1})). PhenBQ content: 2.056 g, 83.1%/mol.

Magnetic Measurements. Room-temperature magnetic measurements were carried out on a Bruker B−E 10B8 magnetometer calibrated with Hg[Co(SCN)$_4$]. EPR spectra were recorded on a JEOL JES−FE/3X spectrometer (HAS) and on a Bruker ESP 300 (UC), both operating at X-band frequency with 100 kHz field modulation.

Crystallographic Structure Determinations. Crystals of Cu(py)$_2$(PhenCat)(PhenBQ) were grown from pyridine solution, crystals of [Cu(tmeda)(diphenate)]$_2$ and [Cu(tmeda)(H_2O)(diphenate)]$_2$ were obtained from acetonitrile solution. Crystals of all three molecules form in the monoclinic crystal system, in the space groups and unit cells

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Table 1. Crystallographic Data for $Cu(py)_2(PhenCat)(PhenBQ)$, Cu(tmeda)(diphenate), and $Cu(tmeda)(H_2O)(diphenate)$[a]

	$Cu(py)_2(PhenCat)(PhenBQ)$	Cu(tmeda)(diphenate)	$Cu(tmeda)(H_2O)(diphenate)$
fw	637.6	430.3	438.0
color	red	blue	blue
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$	$P2_1/n$
a, Å	17.052(3)	17.992(2)	11.457(1)
b, Å	9.165(9)	12.977(2)	9.482(1)
c, Å	19.070(4)	19.005(3)	19.397(2)
β, deg	107.63(2)	107.08(1)	102.73(1)
V, Å^3	2840(2)	4242(1)	2055.4(4)
Z	4	8	4
D_{calcd}, g cm^{-1}	1.492	1.356	1.415
μ, mm^{-1}	0.815	1.057	1.095
T_{max}, T_{min}	0.867, 0.955	0.637, 0.943	0.745, 0.908
R, R_w	0.078, 0.095	0.043, 0.059	0.033, 0.044

[a] Data for all three compounds were collected at room temperature (24−26 °C) using Mo Kα radiation ($\lambda = 0.71073$ Å). Discrepancy indices are defined as: $R = \sum||F_o| - |F|/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

given in Table 1. At the conclusion of the refinement on $[Cu(tmeda)(diphenate)]_2$, a disordered acetonitrile molecule of crystallization was found along the two-fold axis of the space group. Atoms were refined with fractional occupancy factors of 0.5. Tables containing positional and thermal parameters for all atoms, bond lengths and angles, and hydrogen atom locations are available as Supporting Information.

Results

Valence Tautomerism for Quinone Complexes of Copper. Synthetic routes to quinone complexes of copper include direct reactions between metallic copper and the *o*-benzoquinone. When carried out in the presence of an ancillary ligand, L, products are found to have charge distributions that reflect the bonding properties of L. With soft donors and π-acceptor ligands, the complexes have the $L_2Cu^I(SQ)$ charge distribution. Structural characterization on $(PR_3)_2Cu^I(3,6\text{-DBSQ})$ complexes has shown that the metals have the expected tetrahedral coordination geometry,[10] and EPR spectra are typical of organic radicals weakly coupled with the $^{63,65}Cu$ nuclei.[11] Four-coordinate $L_2Cu^{II}(Cat)$ complexes have been characterized structurally with nitrogen-donor ancillary ligands and found to have square planar geometries.[4] EPR spectra are typical of planar Cu(II) complexes with strong g-value anisotropy and strong $^{63,65}Cu$ hyperfine coupling.[11] The difference in charge distribution for four-coordinate complexes containing phosphine and amine (or imine) coligands may be understood as a σ bonding effect that raises the copper dσ orbital energy above the partially occupied semiquinone π orbital. The change in charge distribution results in a consequent shift in the paramagnetic center of the molecule and a shift in the center of nucleophilicity.

With the potential for observations on valence tautomerism for complexes of copper (1), it became of interest to “tune” coligand donation to place metal and quinone orbitals close in energy so that the shift in charge distribution may be induced thermally. Initial experiments carried out with P−N mixed donor ligands led to only $Cu^I(SQ)$ products that exhibited no temperature-dependent shift in EPR signal.[11c] Abakumov has described observations on the solvent-dependence of EPR spectra recorded on a (N−N)Cu(Cat) complex prepared with 4-chloro-3,6-di-*tert*-butylcatechol and di-*tert*-butyl-1,4-diazabutadiene.[12] Spectral changes were interpreted as indicating an equilibrium between $Cu^I(SQ)$ and $Cu^{II}(Cat)$ redox isomers. However, crystallographic characterization on the complex indicated a $[Cu^I(N-N)_2]^+[Cu^{II}(Cat)(SQ)]^-$ ion pair. EPR spectra reported by Dooley and coworkers on the Cu−topaquinone site of an amine oxidase enzyme showed changes in hyperfine coupling that would be consistent with an equilibrium between $Cu^I(TPQ^{SQ})$ and $Cu^{II}(TPQ^{Cat})$ species.[13] This observation has heightened interest in the possibility of valence tautomerism for quinone complexes of copper in a biological system. Kaim has recently reported that complexes of copper prepared with the N−S donor ligand 1-methyl-2-(methylthiomethyl)-1*H*-benzimidazole (mmb) and quinone ligands derived from either 3,5- or 3,6-di-*tert*-butyl-1,2-benzoquinone undergo valence tautomerism in toluene solution.[14] At temperatures below 250 K the spectrum of $Cu^{II}(mmb)(3,5\text{-DBCat})$ is observed, above 250 K the spectrum of $Cu^I(mmb)(3,5\text{-DBSQ})$ appears. In the weakly coordinating solvent THF, the Cu(II) redox isomer is favored, and the spectral change is shifted to higher temperature. While no structural characterization is provided on this compound, it is presumed that the shift in charge distribution is accompanied by a change in coordination geometry, tetrahedral for the Cu(I) isomer and planar for Cu(II).[14]

Valence Tautomerism for Copper Complexes Prepared from 9,10-Phenanthrenequinone. 9,10-Phenanthrenequinone (PhenBQ) reacts slowly with copper wire in acetonitrile solution to form $Cu(PhenSQ)_2$.[8,15] In the presence of tmeda or pyridine, complexes are obtained that have the formula $L_2Cu(PhenQ)_2$, where L_2 = tmeda, 2 py. Crystals of $(py)_2Cu(PhenQ)_2$ form as red pleochroic prisms, and crystals of the tmeda complex are dark green in color. Crystallographic characterization on $(py)_2Cu(PhenQ)_2$ revealed that the molecule has a structure similar to that of (tmeda)Cu(PhenCat)(PhenBQ) (Figure 1). The molecule consists of a planar $(py)_2Cu^{II}(PhenCat)$ unit with a molecule of 9,10-phenanthrenequinone weakly coordinated at the apical site of the Cu paired with the π structure of the

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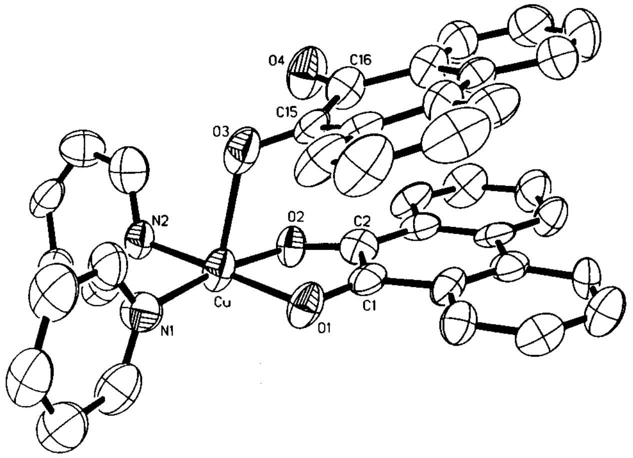


Figure 1. View of the Cu(py)$_2$(PhenCat)(PhenBQ) complex molecule.

Table 2. Selected Bond Distances and Angles for Cu(py)$_2$(PhenCat)(PhenBQ)

	Distances (Å)		
Cu−O1	1.917(9)	Cu−O2	1.927(9)
Cu − O3	2.297(12)	Cu−N1	1.984(12)
Cu−N2	1.976(11)	O1−C1	1.309(17)
O2−C2	1.333(15)	O3−C15	1.252(18)
O4−C16	1.233(15)	C1−C2	1.383(18)
C2−C3	1.415(20)	C3−C4	1.375(17)
C4−C5	1.361(21)	C5−C6	1.384(21)
C15−C16	1.476(20)	C16−C17	1.489(20)
C17−C22	1.366(17)	C22−C23	1.455(21)
C23−C28	1.399(21)	C15−C28	1.436(17)
	Angles (deg)		
O1−Cu−O2	86.5(4)	O1−Cu−O3	83.3(4)
O2−Cu−O3	90.8(4)	O1−Cu−N1	89.6(4)
O2−Cu−N1	171.9(5)	O3−Cu−N1	95.8(4)
O1−Cu−N2	174.8(4)	O2−Cu−N2	89.5(4)
O3−Cu−N2	100.0(4)	N1−Cu−N2	93.9(5)

PhenCat ligand. As with (tmeda)Cu(PhenCat)(PhenBQ), structural features of the quinone ligands fail to point to a clear charge distribution. PhenCat C−O bond lengths, given in Table 2, are slightly shorter than values normally found for catecholate ligands, and the C−O lengths of the apical PhenBQ are slightly longer than benzoquinone double bond values. This is presumably associated with the PhenCat → PhenBQ charge-transfer interaction that binds the ligands together at the metal. Slow recrystallization of both (tmeda)Cu(PhenCat)(PhenBQ) and (py)$_2$Cu(PhenCat)(PhenBQ) from acetonitrile leads to the formation of thin platelike crystals that have proven to be unsuitable for crystallographic characterization. Free 9,10-phenanthrenequinone has been identified in solution from its characteristic absorption at 417 nm. Chemical analyses and EPR spectra obtained by grinding the crystals to powder have been used to identify the complexes formed by PhenBQ dissociation as L$_2$Cu(PhenCat), where L$_2$ = tmeda or 2 py.[15] Samples of (py)$_2$Cu(PhenCat) could also be obtained by slow recrystallization of (tmeda)Cu(PhenCat)(PhenBQ) from a pyridine solution. In our earlier report, (tmeda)Cu(PhenCat)(PhenBQ) was formed in a reaction containing a 1:2 ratio of tmeda to PhenBQ.[8] When carried out with a 1:1 ratio, (tmeda)Cu(PhenCat) is exclusively obtained. The difference in affinity between (tmeda)Cu(PhenCat) and (py)$_2$Cu(PhenCat) for the addition of the apical PhenBQ ligand appears to be related to a temperature-dependent shift in charge distribution in solution.

EPR spectra obtained on the L$_2$Cu(PhenCat) complexes in solution show a dependence on both temperature and solvent. The solution spectrum of (tmeda)Cu(PhenCat) recorded in acetonitrile at room temperature consists of a strongly coupled four-line spectrum, that is typical of square planar Cu(II) complexes [$g_{\mathrm{iso}} = 2.111$, $A_{\mathrm{iso}}(^{63,65}\mathrm{Cu}) = 90.6$ G], and a weakly coupled four line spectrum, [$g_{\mathrm{iso}} = 2.0066$, $A_{\mathrm{iso}} = 9.7$ G] typical of a semiquinone radical chelated to Cu(I) (Figure 2). We tentatively assign these spectra to the (tmeda)Cu$^{\mathrm{II}}$(PhenCat) and (tmeda)Cu$^{\mathrm{I}}$(PhenSQ) redox isomers together in solution. Spectra obtained by either dissolving (tmeda)Cu$^{\mathrm{II}}$(PhenCat) in pyridine, or for solutions of (py)$_2$Cu(PhenCat) dissolved in pyridine at room temperature, also consist of two spectra typical of the Cu(I) and Cu(II) redox isomers. Upon an increase in temperature to 100 °C (Figure 3), the weakly coupled spectrum of (py)$_2$Cu$^{\mathrm{I}}$(PhenSQ) is observed exclusively. A decrease in temperature to −40 °C results in complete disappearance of the weakly coupled spectrum, with only the Cu(II) spectrum of (py)$_2$Cu$^{\mathrm{II}}$(PhenCat) remaining. Additionally, the range over which the spectral change is observed is solvent dependent. A sample of (py)$_2$Cu$^{\mathrm{II}}$(PhenCat) was dissolved in a small quantity of pyridine and diluted with toluene to give a 1:10 pyridine to toluene solution. The shift to the (py)$_2$Cu$^{\mathrm{II}}$(PhenCat) redox isomer was

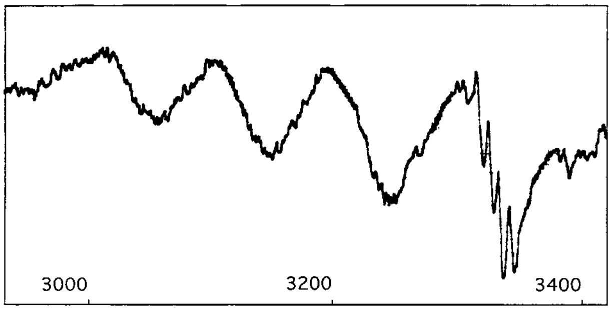


Figure 2. The isotropic EPR spectrum of Cu$^{\mathrm{II}}$(py)$_2$(PhenCat) in pyridine solution at room temperature. Four lines result from coupling to the ^{63,65}Cu nuclei ($I = 3/2$). The spectrum with large hyperfine coupling is associated with the Cu$^{\mathrm{II}}$(py)$_2$(PhenCat) redox isomer; the weakly coupled spectrum results from a small concentration of the Cu$^{\mathrm{I}}$(py)$_2$(PhenSQ) isomer.

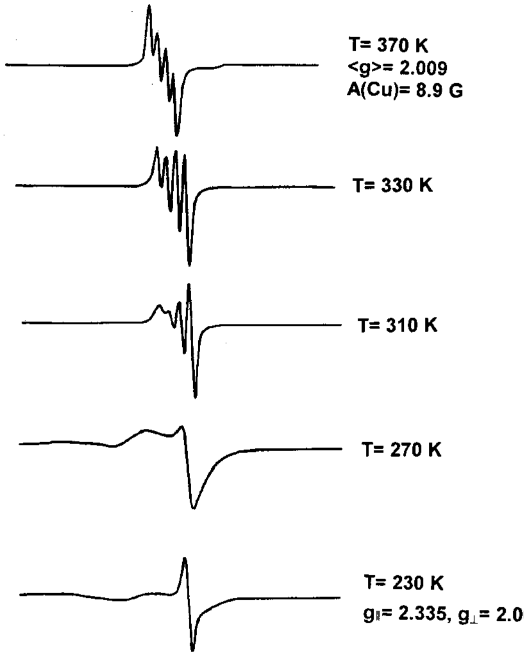


Figure 3. The temperature dependence of the isotropic EPR spectrum of Cu(py)$_2$(PhenQ) in pyridine solution. At 373 K the complex is in the form of the Cu$^{\mathrm{I}}$(py)$_2$(PhenSQ) redox isomer; at 233 K the Cu$^{\mathrm{II}}$(py)$_2$(PhenCat) redox isomer is present exclusively.

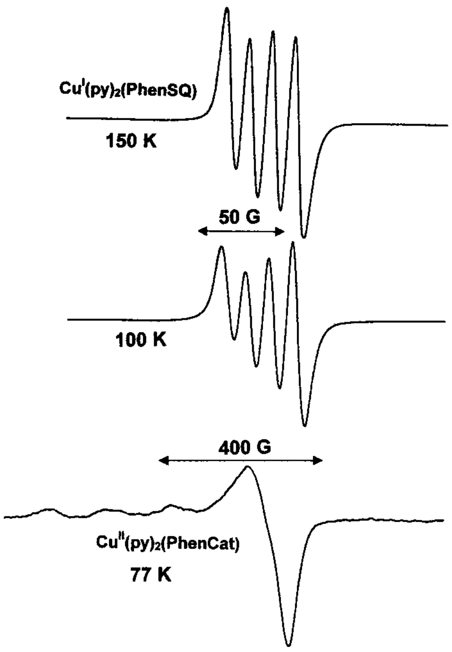


Figure 4. EPR spectra recorded on Cu(py)$_2$(PhenQ) in 1:10 pyridine/toluene solution at 300, 100, and 77 K, showing the transition from Cu^{I}(py)$_2$(PhenSQ) to Cu^{II}(py)$_2$(PhenCat).

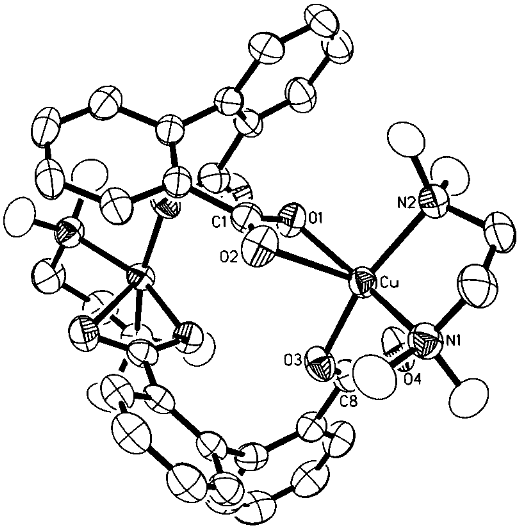


Figure 5. View of the [Cu^{II}(tmeda)(diphenate)]$_2$ dimer resulting from intradiol addition of dioxygen across the interior C−C bond of Cu(tmeda)(PhenQ).

not observed until 100 K for this solution, and at 77 K, the sample consisted exclusively of (py)$_2$Cu^{II}(PhenCat) (Figure 4). These observations are consistent with the conclusion that polar solvents shift the transition to the (py)$_2$Cu^{I}(PhenSQ) redox isomer to higher temperature. Further, the spectral changes observed for the sample in the pyridine/toluene solution occur at temperatures that are well below the freezing point of the solvent mixture. This points to an intramolecular electron-transfer process for the complex that occurs without a gross change in composition or copper coordination geometry.

Aerobic Oxidation of (tmeda)Cu^{I}(PhenSQ). An acetonitrile solution of (tmeda)Cu^{I}(PhenSQ)/(tmeda)Cu^{II}(PhenCat) was observed to consume one molecule of O_2 per complex molecule at room temperature. The resulting green solution was evaporated slowly to give blue crystals. Crystallographic characterization showed the crystals to be the dimeric copper(II) complex of diphenic acid, [(tmeda)Cu^{II}(diphenate)]$_2$ (Figure 5). The diphenic acid presumably results from the addition of dioxygen across the inner C−C bond of the 9,10-phenanthrenediolate ligand. Samples of [(tmeda)Cu^{II}(diphenate)]$_2$, obtained by recrystallization from acetonitrile containing trace quantities of water, formed the hydrate, [(tmeda)Cu^{II}(diphenate)(H$_2$O)]$_2$, shown in Figure 6. In both compounds, the Cu atoms are five coordinate, square pyramidal in structure. Selected bond lengths and angles for both structures are listed in Table 3. For [(tmeda)Cu^{II}(diphenate)]$_2$, the apical coordination site is occupied by oxygen O2 of the chelated carboxylate; for [(tmeda)Cu^{II}(diphenate)(H$_2$O)]$_2$, O3 occupies the apical position. Structural constraints of the diphenate ligand prevent chelation to a single metal. A twist between planes of phenyl rings leads to the bridged dimeric structure that appears for the ring-opened oxidation products.

In an attempt to isolate the intermediate formed upon dioxygen addition, the reaction was carried out in acetonitrile at 0 °C (Scheme 1). Under these conditions, a green microcrystalline solid separated from the solution as dioxygen was added to the flask. An attempted recrystallization of this product

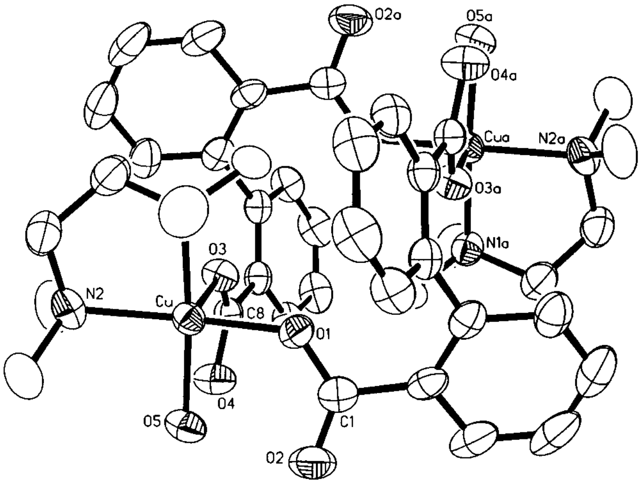
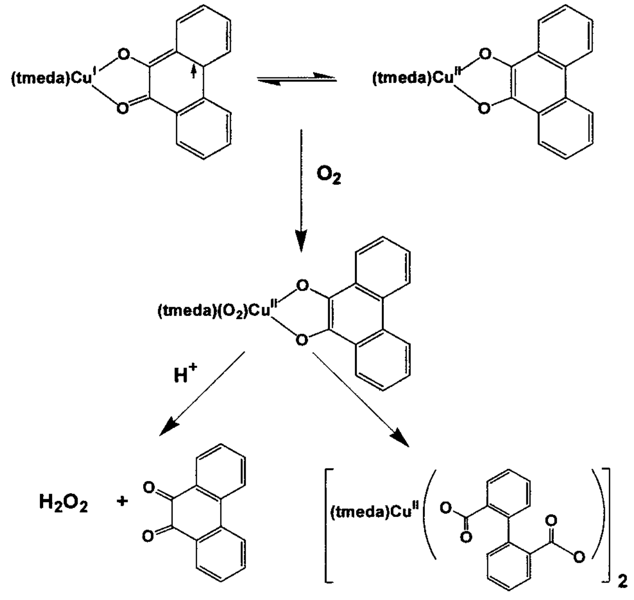


Figure 6. View of the [Cu^{II}(tmeda)(H$_2$O)(diphenate)]$_2$ dimer.

Table 3. Selected Bond Distances and Angles for [Cu(tmeda)(diphenate)]$_2$ and [Cu(tmeda)(H$_2$O)(diphenate)]$_2$

	[Cu(tmeda)(diphenate)]$_2$		
	Distances (Å)		
Cu−O1	1.979(2)	Cu−O2	2.407(3)
Cu−O3	1.930(3)	Cu−N1	2.039(3)
Cu−N2	2.033(3)	O1−C1	1.277(4)
O2−C2	1.251(5)	O3−C8	1.265(5)
O4−C8	1.232(5)		
	Angles (deg)		
O1−Cu−O2	59.6(1)	O1−Cu−O3	93.1(1)
O2−Cu−O3	95.9(1)	O1−Cu−N1	160.9(1)
O2−Cu−N1	101.9(1)	O3−Cu−N1	93.6(1)
O1−Cu−N2	92.7(1)	O2−Cu−N2	103.1(1)
O3−Cu−N2	160.5(1)	N1−Cu−N2	86.8(1)
	[Cu(tmeda)(H$_2$O)(diphenate)]$_2$		
	Distances (Å)		
Cu−O1	2.006(2)	Cu−O3	2.193(2)
Cu−O5	1.983(3)	Cu−N1	1.999(3)
Cu−N2	2.094(3)	O1−C1	1.265(4)
O2−C1	1.246(4)	O3−C8	1.257(4)
O4−C8	1.251(4)		
	Angles (deg)		
O1−Cu−O3	100.9(1)	O1−Cu−O5	94.0(1)
O3−Cu−O5	92.5(1)	O1−Cu−N1	88.0(1)
O3−Cu−N1	93.0(1)	O5−Cu−N1	173.6(1)
O1−Cu−N2	159.9(1)	O3−Cu−N2	98.5(1)
O5−Cu−N2	90.6(1)	N1−Cu−N2	85.4(1)

Scheme 1



from acetonitrile led to a color change to bright blue, with formation of the diphenic acid complex described above. The peroxide content of the product formed initially was determined by an iodometric titration. The result indicated a nearly stoichiometric quantity of peroxide (96.5%) per (tmeda)Cu(PhenCat) monomer. A second analysis for PhenBQ was carried out to determine whether ring cleavage had occurred. This result indicated that the PhenCat ligand (obtained in the analysis as PhenBQ) was intact. The low solubility of the deoxygenated product has precluded a solution study of aerobic oxidation, but changes in infrared spectrum that occur with the formation of the product, tentatively identified as (tmeda)Cu(O_2)(PhenQ), and rearrangement to form the [(tmeda)Cu(diphenate)$]_2$ dimer have been recorded on solid samples and are shown in Figure 7. Recent structural characterization on complexes containing the stable peroxyphenanthrenesemiquinone ligand may point to the formation of a peroxysemiquinone intermediate upon initial addition of O_2 to the (tmeda)Cu^{II}(PhenCat)/(tmeda)Cu^{I}(PhenSQ) mixture. However, the low solubility of the isolated product is perhaps more consistent with a polymeric material containing bridging peroxo groups.

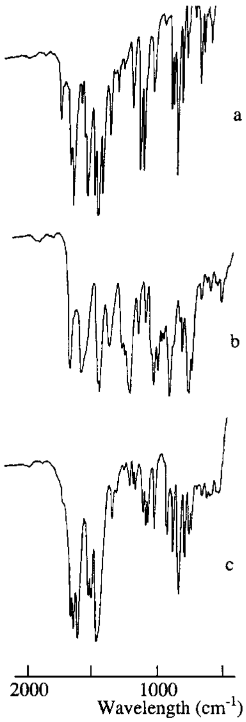


Figure 7. Solid state (KBr) infrared spectra recorded on a) (tmeda)-Cu(PhenCat), b) (tmeda)Cu(O_2)(PhenQ), and c) [(tmeda)Cu(diphenate)$]_2$.

Discussion

The temperature-dependent changes in EPR spectra for (tmeda)Cu(PhenQ) are associated with a reversible shift in charge distribution (1). Observations on spectral shifts in frozen solutions cast doubt on an accompanying structural change between planar Cu(II) and tetrahedral Cu(I) redox isomers. The complex may have a “crushed-tetrahedral” structure that would accommodate the metal ion in either oxidation state. It is of interest to compare the Cu^{II}(PhenCat)/Cu^{I}(PhenSQ) equilibrium to the Co^{III}(Cat)/Co^{II}(SQ) and $Mn^{IV}(Cat)_2/Mn^{II}(SQ)_2$ equilibria.[1] In these cases, the thermodynamic changes that define equilibrium conditions arise from a shift in composition of the metal $d\sigma$ orbitals directed at ligand coordination sites. The magnitude of the effect for copper would be considerably less since there is at least partial occupancy of this orbital in either structure. However, the change in acidity that occurs with the metal reduction process disfavors coordination by the hard nitrogen and oxygen donor ligands. Copper(I) tmeda complexes have Cu−N lengths in the range of 2.09 Å,[16] and recent structures on Cu(I)−semiquinone complexes show Cu−O lengths of 2.08 Å.[10] Copper−oxygen bond lengths increase by 0.1 Å with the shift in charge distribution to the Cu^{I}(SQ) redox isomer, and the Cu−N bonds to the tmeda nitrogens increase by 0.05 Å. While this change is clearly smaller than bond length changes that occur for the ls Co(III)/hs Co(II) and d^3 Mn(IV)/hs d^5 Mn(II) equilibria (~0.2 Å), it is evidently sufficient to provide the positive changes in enthalpy and entropy that define the thermal conditions for the Cu^{II}(Cat)/Cu^{I}(SQ) equilibrium.

Early models for catechol oxidation by the catechol dioxygenase enzymes contained shifts in charge distribution involving Fe^{III}(Cat) and Fe^{II}(SQ) redox isomers,[17] and it is of interest to consider the importance of valence tautomerism for the copper systems. While the shift in charge distribution might influence the point of O_2 addition, the overall nucleophilicity of the complex molecule remains essentially unchanged. Examples of O_2 activation by coordination with a nucleophilic metal are relatively common, basic solutions of catechol are notoriously oxygen sensitive,[18] and the peroxosemiquinone complexes appear to form by direct O_2 addition to the coordinated catecholate (or diolate) ligand.[6,7] Either the reduced metal or the catecholate form of the ligand may be the site of initial O_2 attack. Steps in the rearrangement of the peroxo species formed initially to give the dicarboxylate complex are of interest, and the present system may offer the opportunity for study of this process under controlled conditions of temperature and solvent.

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T032929 (A.R.)). C.G.P. and G.S. would like to thank the US–Hungarian Joint Fund for collaborative research support through grant 098/91.

Supporting Information Available: Complete tables of crystallographic data, final atomic coordinates, bond lengths and angles, and hydrogen atom coordinates for Cu(py)$_2$(PhenCat)(PhenBQ), [Cu(tmeda)(diphenate)]$_2$, and [Cu(tmeda)(H$_2$O)(diphenate)]$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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