

# Iminosemiquinone Complexes of Copper: Structural, Magnetic, and Electrochemical Characterization of Complexes of the Phenoxazinolate Semiquinone Radical

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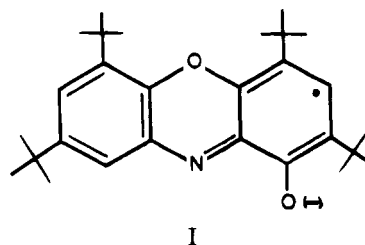
Iminosemiquinone complexes of copper have been prepared by treating Cu metal with 2,4,6,8-tetra-*tert*-butylphenoxazin-1-one (PhenoxBQ). Reactions carried out with PPh<sub>3</sub> gave Cu<sup>I</sup>(PPh<sub>3</sub>)<sub>2</sub>(PhenoxSQ). Crystallographic characterization of crystals obtained as the acetonitrile solvate (triclinic, *P*1, *a* = 11.414(2) Å, *b* = 15.431(2) Å, *c* = 17.999(3) Å,  $\alpha$  = 92.88(1)°,  $\beta$  = 94.21(1)°,  $\gamma$  = 109.84(1)°, *V* = 2964.4(8) Å<sup>3</sup>, *Z* = 2, *R* = 0.064) has shown that the coordination geometry is tetrahedral, EPR spectra indicate that the unpaired electron is ligand-based, and electrochemical properties consist of one-electron oxidation and reduction reactions at the iminoquinone ligand. Reactions carried out in the absence of coligand or in the presence of a nitrogen-donor coligand gave Cu<sup>II</sup>(PhenoxSQ)<sub>2</sub>. Crystallographic characterization of crystals obtained as the dichloromethane solvate (monoclinic, *C*2/*c*, 28.40(2) Å, 12.946(4) Å, *a* = 20.552(12) Å,  $\beta$  = 129.32(4)°, *V* = 5846(6) Å<sup>3</sup>, *R* = 0.070) has shown that the molecule has a distorted tetrahedral structure. Electrochemical characterization has indicated that the complex undergoes two one-electron oxidations and two one-electron reductions, all occurring at the iminoquinone ligands. EPR spectra and variable-temperature magnetic measurements indicate that exchange between PhenoxSQ ligands is ferromagnetic, while Cu–PhenoxSQ exchange is antiferromagnetic. At low temperature, the complex has a ligand-based *S* = 1/2 magnetic ground state.

## Introduction

Iminoquinone complexes of the transition metals are of interest as systems that combine electrochemically active ligands with metals that typically have one or two readily accessible oxidation states.<sup>2</sup> Quinone and quinoid cofactors appear in biological systems and sometimes function in conjunction with a redox-active metal center.<sup>3</sup> Biopterins, that include 6-tetrahydrobiopterin, serve as cofactors with the non-heme iron centers of pterin-dependent hydroxylase enzymes that include tryptophan hydroxylase, tyrosine hydroxylase, and phenylalanine hydroxylase (PAH).<sup>4</sup> A bacterial form of PAH was discovered that contained copper at the active site, rather than iron.<sup>5</sup> EPR and EXAFS have been useful in providing information on changes that exist in oxidized and reduced forms of *Chromobacterium violaceum* PAH that may be relevant to the mechanism of dioxygen activation and substrate oxidation.<sup>6</sup> Pterin–copper coordination appears to occur in, at least, the oxidized form of the enzyme. With this observation came model studies on copper–pterin complexes, although nearly all have been carried out with the aromatic oxidized pterins rather than the

redox-active reduced pterins.<sup>7</sup> Reduced pterins that resemble the cofactor molecules are difficult to synthesize and are subject to irreversible tautomeric shifts in bonding that complicate their solution chemistry.<sup>8</sup>

Complexes of the phenoxazinolate semiquinone radical (I,



PhenoxSQ) have been studied with iron, nickel, and ruthenium to investigate the coordination properties of iminosemiquinone ligands.<sup>2,9,10</sup> The electrochemical properties of these compounds show that the iminoquinone ligands, rather than the metal ion, are the centers of redox activity within the potential range  $\pm 1.5$  V. It has been noted that the PhenoxBQ and PhenoxSQ ligands have structural and electrochemical features in common with the partially reduced biopterins.<sup>2,9</sup> PhenoxSQ complexes of iron may resemble partially reduced iron–biopterin species, and the PhenoxSQ complexes of copper may serve as models for Cu–biopterin complexes. In the present paper, we describe PhenoxSQ complexes that have been investigated to provide characterization on iminoquinone complexes of copper.

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- (1) (a) University of Veszprem. (b) University of Colorado.
- (2) Whalen, A. M.; Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.* **1994**, *33*, 347.
- (3) See for example: *Principles and Applications of Quinoproteins*; Davidson, V. L., Ed.; Marcel Dekker, Inc.: New York, 1992.
- (4) (a) Kaufman, S.; Kaufman, E. S. In *Folates and Pterins*; Blakely, R. L., Benkovic, S. J., Eds.; John Wiley, Inc.: New York, 1985; Vol. 2, p 251. (b) Andersson, K. K.; Cox, D. D.; Que, L., Jr.; Flatmark, T.; Haavik, J. J. *Biol. Chem.* **1988**, *263*, 18621. (c) Dix, T. A.; Benkovic, S. J. *Acc. Chem. Res.* **1988**, *21*, 101.
- (5) (a) Pember, S. O.; Benkovic, S. J.; Villafranca, J. J.; Pasenkiewicz-Gierula, M.; Antholine, W. E. *Biochemistry* **1987**, *26*, 4477. (b) Pember, S. O.; Johnson, K. A.; Villafranca, J. J.; Benkovic, S. J. *Biochemistry* **1989**, *28*, 2124. (c) Blackburn, N. J.; Strange, R. W.; Carr, R. T.; Benkovic, S. J. *Biochemistry* **1992**, *31*, 5298.
- (6) Blackburn, N. J. In *Bioinorganic Chemistry of Copper*; Karlin, K. D., Tyeklar, Z., Eds.; Chapman and Hall: New York, 1993; p 164.

(7) Yamauchi, O.; Odani, A.; Masuda, H.; Funahashi, Y. In *Bioinorganic Chemistry of Copper*; Karlin, K. D., Tyeklar, Z., Eds.; Chapman and Hall: New York, 1993; p 363.

(8) Eberlein, G.; Bruice, T. C.; Lazarus, R. A.; Henrie, R.; Benkovic, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 7916.

(9) (a) Bhattacharya, S.; Pierpont, C. G. *J. Am. Chem. Soc.* **1990**, *112*, 4561. (b) Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.* **1992**, *31*, 2020.

(10) Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.* **1994**, *33*, 6038.

**Table 1.** Crystallographic Data for  $\text{Cu}(\text{PPh}_3)_2(\text{PhenoxSQ})$  and  $\text{Cu}(\text{PhenoxSQ})_2 \cdot \text{CH}_2\text{Cl}_2^a$ 

	$\text{Cu}(\text{PPh}_3)_2(\text{PhenoxSQ})$	$\text{Cu}(\text{PhenoxSQ})_2$
mol wt	1042.2	990.7
color	red-brown	purple
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$
$a$ , Å	11.414(2)	28.403(18)
$b$ , Å	15.431(2)	12.946(4)n
$c$ , Å	17.999(3)	20.552(12)
$\alpha$ , deg	92.88(1)	90.00
$\beta$ , deg	94.21(1)	129.32(4)
$\gamma$ , deg	109.84(1)	90.00
vol, Å <sup>3</sup>	2964.4(8)	5846(6)
$Z$	2	4
$D_{\text{calcd}}$ , g cm <sup>-3</sup>	1.141	1.126
$\mu$ , mm <sup>-1</sup>	0.461	0.506
$R$ , $R_w$	0.064, 0.080	0.070, 0.099
GOF	1.75	1.25

<sup>a</sup> Radiation Mo K $\alpha$  ( $\lambda$  0.710 73 Å); temperature 293–298 K.  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$ .

## Experimental Section

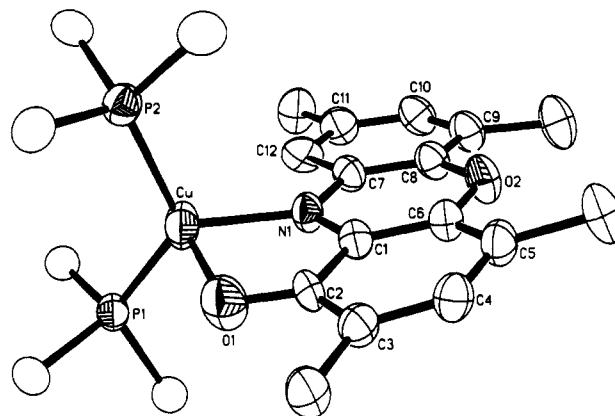
**Materials.** 2,4,6,8-Tetra-*tert*-butylphenoxazin-1-one (PhenoxBQ) was prepared according to a literature procedure.<sup>11</sup>

**$\text{Cu}(\text{PPh}_3)_2(\text{PhenoxSQ})$ .** A mixture of PhenoxBQ (0.421 g, 1.0 mmol), copper powder (0.064 g, 1.0 mmol), and  $\text{PPh}_3$  (0.525 g, 2.0 mmol) in 20 mL of acetonitrile was refluxed under argon for 3 h to give a red-brown solution. The volume of the solution was reduced to give red-brown crystals of  $\text{Cu}(\text{PPh}_3)_2(\text{PhenoxSQ})$  (0.68 g) in 67% yield. Anal. Calcd for  $\text{C}_{64}\text{H}_{69}\text{N}_2\text{P}_2\text{Cu}$ : C, 76.1; H, 6.9; N, 1.4. Found: C, 76.5; H, 6.6; N, 1.7.

**$\text{Cu}(\text{PhenoxSQ})_2$ .** A mixture of PhenoxBQ (0.421 g, 1.0 mmol) and copper powder (0.032 g, 0.5 mmol) in 15 mL of acetonitrile was refluxed for 5 h under argon to give a dark brown solution and a black solid. The solid was extracted with dichloromethane to give dark brown crystals of  $\text{Cu}(\text{PhenoxSQ})_2$  (0.655 g) in 74% yield as a  $\text{CH}_2\text{Cl}_2$  solvate. Anal. Calcd for  $\text{C}_{56}\text{H}_{78}\text{N}_2\text{O}_4\text{Cu}$ : C, 74.2; H, 8.7; N, 3.1. Found: C, 74.3; H, 10.9; N, 3.4.

**Physical Measurements.** Electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. Infrared spectra were recorded on an IBM IR/30 FTIR spectrometer with samples prepared as KBr pellets. EPR spectra were recorded on a Bruker ESP-300E spectrometer and referenced to DPPH as the  $g$  value standard. Spectra were recorded at X-band frequency and are displayed in Figures 3 and 7 as first-derivative spectra. <sup>1</sup>H NMR spectra were recorded on a Varian VXR 300s spectrometer. Magnetic measurements were made on a Quantum Design MPMS-5 SQUID magnetometer. Cyclic voltammograms were obtained with a Cypress CYSY-1 computer-controlled electroanalysis system. A  $\text{Ag}/\text{Ag}^+$  reference electrode was used that consisted of a  $\text{CH}_3\text{CN}$  solution of  $\text{AgPF}_6$  in contact with a silver wire placed in glass tubing with a Vycor frit at one end to allow ion transport. Tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte, and the  $\text{Fc}/\text{Fc}^+$  couple was used as an internal standard.

**Crystallographic Structure Determination of  $\text{Cu}(\text{PPh}_3)_2(\text{PhenoxSQ})$ .** A red-brown parallelepiped of dimensions  $0.48 \times 0.27 \times 0.18$  mm obtained by slow evaporation of an acetonitrile solution was mounted and aligned on a Siemens P3 diffractometer. Axial photographs indicated only triclinic symmetry, and the centered settings of 25 reflections gave the unit cell dimensions listed in Table 1. Data were collected by  $\theta$ - $2\theta$  scans within the angular range  $3.0$ – $45.0^\circ$ . The results of  $\psi$  scans indicated that absorption was negligible, and no correction was applied. The structure was solved using a Patterson map. At the conclusion of preliminary refinement, a disordered acetonitrile solvate molecule was located about the crystallographic inversion center at  $0, 0, 1/2$ . Final cycles of refinement included fixed contributions for hydrogen atoms converged with discrepancy indices of  $R = 0.064$  and  $R_w = 0.080$ . Tables containing atom positions, anisotropic displacement parameters, hydrogen atom locations, and bond lengths and angles are available as supplementary material.



**Figure 1.** View of the  $\text{Cu}(\text{PPh}_3)_2(\text{PhenoxSQ})$  molecule.

**Crystallographic Structure Determination of  $\text{Cu}(\text{PhenoxSQ})_2$ .** A purple-brown tabular crystal of dimensions  $0.68 \times 0.40 \times 0.22$  mm obtained by slow evaporation of a dichloromethane solution was coated with an amorphous resin to retard decay. Axial photographs indicated monoclinic symmetry, and the centered settings of 25 reflections gave the unit cell dimensions listed in Table 1. Data were collected by  $\theta$ - $2\theta$  scans within the angular range  $3.0$ – $45.0^\circ$ . Crystals were observed to diffract weakly, often an indication of disorder. Consequently, the crystal chosen for data collection was relatively large. The results of  $\psi$  scans indicated that absorption was negligible, and no correction was applied. The structure was solved using a Patterson map. At the conclusion of preliminary refinement, a disordered dichloromethane solvate molecule was located and included in further refinement. Final cycles of refinement including fixed contributions for hydrogen atoms converged with discrepancy indices of  $R = 0.070$  and  $R_w = 0.099$ . Tables containing atom positions, anisotropic displacement parameters, hydrogen atom locations, and bond lengths and angles are available as supplementary material.

## Results

$\sigma$ -Benzoquinones react oxidatively with copper metal to give bis(semiquinonato)copper(II) complexes.<sup>12</sup> In the presence of a phosphine coligand tetrahedral  $\text{Cu}^{\text{I}}(\text{PR}_3)_2(\text{SQ})$  products are obtained, with nitrogen-donor coligands planar or dimeric  $\text{Cu}^{\text{II}}(\text{N-N})(\text{Cat})$  products form, and coligand bonding directs the charge distribution within the copper-quinone chelate ring.<sup>13</sup> Similar reactions have been investigated with the iminoquinone PhenoxBQ. Reactions carried out in the presence of triphenylphosphine have been found to give  $\text{Cu}^{\text{I}}(\text{PPh}_3)_2(\text{PhenoxSQ})$ . In the absence of coligand, the product obtained is  $\text{Cu}^{\text{II}}(\text{PhenoxSQ})_2$ , and this is also the product of reactions carried out with pyridine, 2,2'-bipyridine, and 1,10-phenanthroline coligands. Both complexes have been fully characterized, and the results of this investigation are described below.

**$\text{Cu}(\text{PPh}_3)_2(\text{PhenoxSQ})$ .** Crystallographic characterization has shown that  $\text{Cu}(\text{PPh}_3)_2(\text{PhenoxSQ})$  is tetrahedral. A view of the coordination geometry is given in Figure 1, and selected bond lengths and angles are listed in Table 2. The  $\text{O1}-\text{Cu}-\text{N1}$  angle within the chelate ring is  $77.9(2)^\circ$ , the  $\text{P1}-\text{Cu}-\text{P2}$  angle is opened to  $124.3(1)^\circ$ , and the dihedral angle between the  $\text{O1}-\text{Cu}-\text{N1}$  and  $\text{P1}-\text{Cu}-\text{P2}$  planes is  $84.2^\circ$ . The  $\text{Cu}-\text{O}$  length is  $0.1$  Å longer than the  $\text{Cu}-\text{N}$  length. This appears to be a feature, associated with PhenoxSQ complexes of nucleo-

(12) (a) Muraev, V. A.; Cherkasov, V. K.; Abakumov, G. A.; Razuvaev, G. A. *Dokl. Akad. Nauk SSSR* **1977**, *236*, 620. (b) Razuvaev, G. A.; Cherkasov, V. K.; Abakumov, G. A. *J. Organomet. Chem.* **1978**, *160*, 361. (c) Speier, G.; Tyeklar, Z.; Szabo, L., II; Toth, P.; Pierpont, C. G.; Hendrickson, D. N. *The Activation of Dioxxygen and Homogeneous Catalytic Oxidation*; Barton, H. D., Martell, A. E., Sawyer, D. T., Eds.; Plenum: New York, 1993; p 423. (d) Speier, G. *New J. Chem.* **1994**, *18*, 143.

(13) Pierpont, C. G.; Lange, C. W. *Prog. Inorg. Chem.* **1994**, *41*, 331.

(11) Stegmann, H. B.; Scheffler, K. *Chem. Ber.* **1968**, *101*, 262.

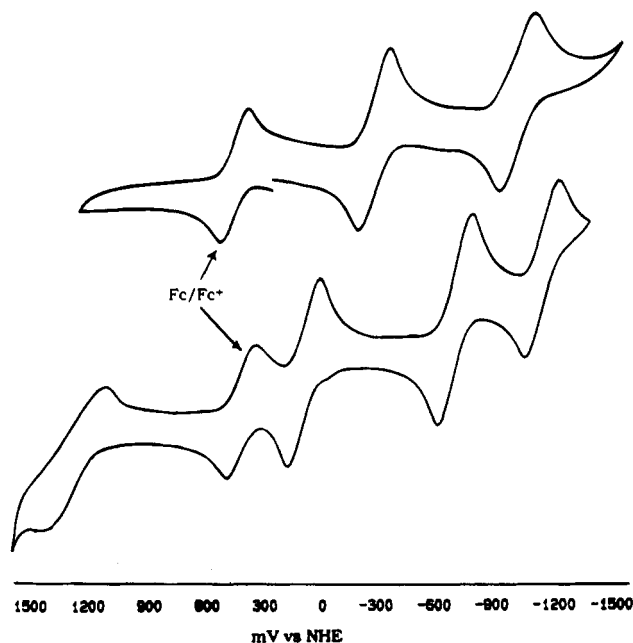
**Table 2.** Selected Bond Lengths and Angles for  $\text{Cu}(\text{PPh}_3)_2(\text{PhenoxSQ})$ 

Bond Lengths (Å)			
Cu-P1	2.223(2)	C2-C3	1.395(11)
Cu-P2	2.273(2)	C3-C4	1.388(11)
Cu-O1	2.131(6)	C4-C5	1.412(10)
Cu-N1	2.003(6)	C5-C6	1.372(11)
N1-C1	1.348(10)	C1-C6	1.413(11)
O1-C2	1.287(10)	N1-C7	1.392(8)
C1-C2	1.436(9)	C6-O2	1.407(8)
Angles (deg)			
P1-Cu-P2	124.3(1)	P1-Cu-O1	106.8(2)
P2-Cu-O1	99.5(1)	P1-Cu-N1	123.4(1)
P2-Cu-N1	109.5(1)	O1-Cu-N1	77.9(2)

philic metals. Distances to the Fe(III) ion of  $\text{FeCl}(\text{PhenoxSQ})_2$  and the Ni(II) center of  $\text{Ni}(\text{PhenoxSQ})_2$  showed a pattern where the M-O distance was greater than 0.1 Å shorter than the M-N length.<sup>2</sup> Bond lengths within the PhenoxSQ ligand are indicative of its semiquinone charge. The C1-O1, C2-N, and C1-C2 lengths are all consistent with values found for PhenoxSQ ligands in other structure determinations and differ diagnostically from PhenoxBQ values.<sup>9</sup> Infrared bands at 1512 and 1478  $\text{cm}^{-1}$  are associated with the PhenoxSQ C-O and C-N bonds; related bands appear at 1534 and 1480  $\text{cm}^{-1}$  for  $\text{FeCl}(\text{PhenoxSQ})_2$ . Two other bands that appear characteristically for PhenoxSQ are found at 1042 and 1071  $\text{cm}^{-1}$  and may be due to C-C bond deformations in the quinone ring of the ligand. The intense red color of  $\text{Cu}(\text{PPh}_3)_2(\text{PhenoxSQ})$  is due to a strong electronic transition that appears at 398 nm ( $16 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ). The PhenoxSQ ligand of  $\text{Cu}(\text{PPh}_3)_2(\text{PhenoxSQ})$  undergoes reversible oxidation at -0.333 V (vs NHE) and reduction at -1.064 V, as shown in Figure 2. Potentials for these reactions are shifted positively by more than 0.5 V relative to the PhenoxBQ/PhenoxSQ<sup>-</sup> and PhenoxSQ<sup>-</sup>/PhenoxCat<sup>2-</sup> couples of the free ligand.<sup>9b</sup> Magnetic measurements show that  $\text{Cu}(\text{PPh}_3)_2(\text{PhenoxSQ})$  has a single unpaired electron, and the EPR spectrum of the complex, shown in Figure 3, indicates that spin density is concentrated on the PhenoxSQ ligand. The spectrum is centered about a *g* value of 2.004, and it has been simulated with coupling constants of 9.9 and 10.6 G for the <sup>63</sup>Cu and <sup>65</sup>Cu nuclei, 14.6 G for two equivalent P nuclei, 7.0 G for the PhenoxSQ nitrogen, and 1.58 G for three nominally equivalent PhenoxSQ ring hydrogen atoms. Values for couplings to the metal and phosphorus nuclei are similar to those used in the spectral simulation of  $\text{Cu}(\text{PPh}_3)_2(3,5\text{-DBSQ})$ .<sup>12</sup>

**Cu(PhenoxSQ)<sub>2</sub>.** Reactions carried out between copper metal and PhenoxBQ in acetonitrile solution led to the formation of  $\text{Cu}(\text{PhenoxSQ})_2$ . Structural characterization has shown that the metal is in a distorted tetrahedral coordination environment with a dihedral angle of 49.9° between ligand planes. A view of the complex molecule is given in Figure 4, and selected bond lengths and angles are listed in Table 3. The distortion of  $\text{Cu}(\text{PhenoxSQ})_2$  toward a planar structure is greater with copper than found earlier for  $\text{Ni}(\text{PhenoxSQ})_2$ , where the dihedral angle between ligand planes was 72.0°. Otherwise, Cu-O and Cu-N lengths are slightly longer than the Ni-O and Ni-N lengths of 1.905(5) and 1.908(6) Å, and structural features of the PhenoxSQ ligands are similar to those of  $\text{Ni}(\text{PhenoxSQ})_2$ ,  $\text{FeCl}(\text{PhenoxSQ})_2$ ,  $\text{Ru}(\text{CO})_2(\text{PhenoxSQ})_2$ , and  $\text{Cu}(\text{PPh}_3)_2(\text{PhenoxSQ})$ .

Optical spectra of  $\text{Cu}(\text{PhenoxSQ})_2$  both in dichloromethane solution and in the solid state as a KBr pellet consist of a series of sharp transitions at  $\lambda$  382 nm ( $\epsilon = 10\,500 \text{ M}^{-1} \text{ cm}^{-1}$ ), 404 (9500), 478 (3250), and 522 (3800) in the high-energy region (Figure 5), with broad transitions at 800 (3700) and 1290 nm (1100) in the low-energy region of the spectrum. A similar spectrum was observed for  $\text{Ni}(\text{PhenoxSQ})_2$  in the high-energy

**Figure 2.** Cyclic voltammograms of  $\text{Cu}(\text{PPh}_3)_2(\text{PhenoxSQ})$  (top) and  $\text{Cu}(\text{PhenoxSQ})_2$  (bottom) recorded in dichloromethane.

region, but with the absence of the 1290 nm transition in the near-IR. Infrared bands that are associated characteristically with PhenoxSQ appear at 1525 and 1481  $\text{cm}^{-1}$ , and the two bands at lower energy that are particularly sensitive to ligand charge appear at 1046 and 1081  $\text{cm}^{-1}$ .

Redox chemistry may occur at either the metal or the iminosemiquinone ligands of  $\text{Cu}(\text{PhenoxSQ})_2$ . Electrochemical characterization gave the four-couple series, shown in Figure 2, consisting of two reversible or quasireversible oxidations and reductions. Oxidations appear at +1.20 and +0.076 V; reductions, at -0.704 and -1.140 V. Values for potentials and the general appearance of the CV are similar to those for the redox series of  $\text{Ni}(\text{PhenoxSQ})_2$ ,  $\text{FeCl}(\text{PhenoxSQ})_2$ , and  $\text{Ru}(\text{CO})_2(\text{PhenoxSQ})_2$ . All four couples are ligand-based, and there is no evidence for further reduction of the metal ion to a potential of -1.5 V (vs NHE). A third reduction was observed for  $\text{FeCl}(\text{PhenoxSQ})_2$  at -1.427 V that occurs at the metal; reduction of the Cu center of  $\text{Cu}(\text{PhenoxSQ})_2$  must occur at a somewhat more negative potential.

**Magnetism and Magnetic Resonance Spectra of  $\text{Cu}(\text{PhenoxSQ})_2$ .** Because  $\text{Cu}(\text{PhenoxSQ})_2$  is a complex consisting of two radical ligands coordinated to a  $S = 1/2$  paramagnetic metal ion, its magnetic properties are of interest. Magnetic measurements, recorded as a function of temperature, give the results shown in Figure 6. At 5 K the magnetic moment is  $1.53 \mu_B$ , slightly below the  $S = 1/2$  value. The magnetic moment increases steadily with increasing temperature to a value of  $2.50 \mu_B$  at 350 K. The net exchange interaction is antiferromagnetic with a  $S = 1/2$  ground state; population of the  $S = 3/2$  excited state is responsible for the temperature-dependent behavior. If the structure of the molecule was more regularly tetrahedral, with a 90° angle between ligand planes, the interaction between orthogonal ligand spins would likely be weak and ferromagnetic. Exchange between the metal spin and the ligands would be relatively strong and antiferromagnetic since the metal  $t_2$  orbital is of both  $\sigma$  and  $\pi$  symmetries. Antiferromagnetic metal-radical exchange results in a diamagnetic spin state for  $\text{Ni}(\text{PhenoxSQ})_2$ . If this were the dominant effect for  $\text{Cu}(\text{PhenoxSQ})_2$ , ground state spin density would be concentrated on one of the PhenoxSQ ligands and the complex would suffer from radical spin frustration.

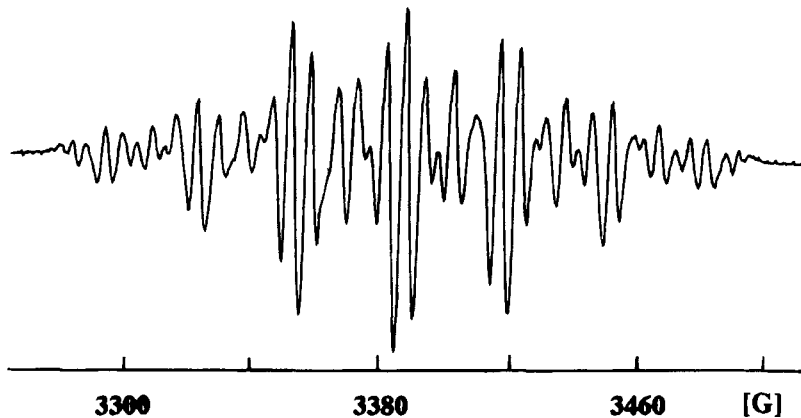


Figure 3. EPR spectrum of  $\text{Cu}(\text{PPh}_3)_2(\text{PhenoxSQ})$  recorded in toluene at room temperature.

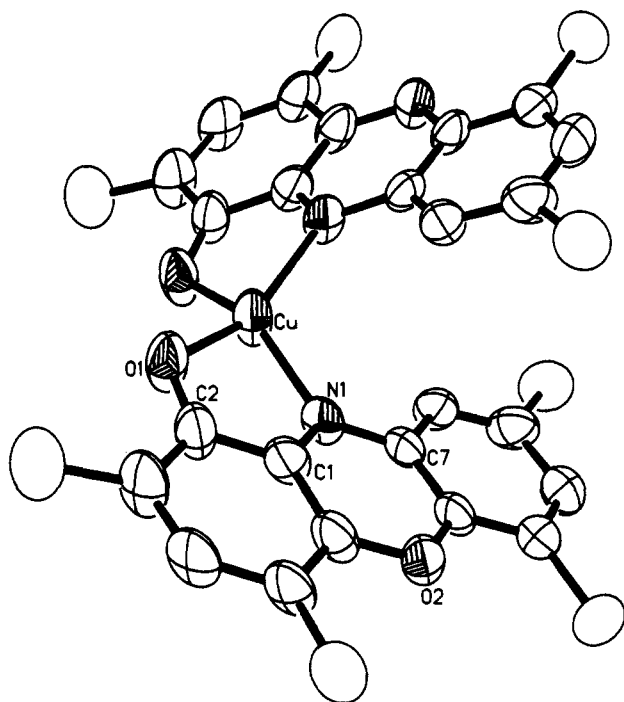


Figure 4. View of the  $\text{Cu}(\text{PhenoxSQ})_2$  molecule. The dihedral angle between ligand planes is  $49.9^\circ$ .

Table 3. Selected Bond Lengths and Angles for  $\text{Cu}(\text{PhenoxSQ})_2$

Bond Lengths (Å)			
Cu—O1	1.920(7)	C3—C4	1.377(12)
Cu—N1	1.933(6)	C4—C5	1.397(15)
N1—C1	1.345(12)	C5—C6	1.384(13)
O1—C2	1.295(9)	C1—C6	1.447(11)
C1—C2	1.432(14)	N1—C7	1.374(12)
C2—C3	1.402(14)	C6—O2	1.377(12)
Angles (deg)			
O1—Cu—N1	83.3(3)	O1—Cu—O1'	101.0(3)
N1—Cu—N1'	113.7(3)	O1—Cu—N1'	144.3(3)

As a second model for spin coupling, the complex may be viewed to have a distorted planar structure. In a regular planar geometry with a dihedral angle of  $0^\circ$  between ligand planes, radical spins would couple antiferromagnetically, and the remaining metal spin, in an orthogonal  $\sigma$  orbital ( $d_{x^2-y^2}$ ), would be the ground state paramagnetic center of the molecule. The diamagnetism of the planar  $\text{M}(3,5\text{-DBSQ})_2$  ( $\text{M} = \text{Pd}, \text{Pt}$ ) and  $\text{Ni}(3,6\text{-DBSQ})_2$  complexes is consistent with this model, and  $\text{Cu}(3,6\text{-DBSQ})_2$  has a metal-based  $S = 1/2$  magnetic moment, as is evident from the anisotropy in its  $g$  tensor.<sup>14,15</sup> Structural characterization of  $\text{Cu}(3,6\text{-DBSQ})_2$  has shown that the metal lies at a crystallographic inversion center, requiring rigorous

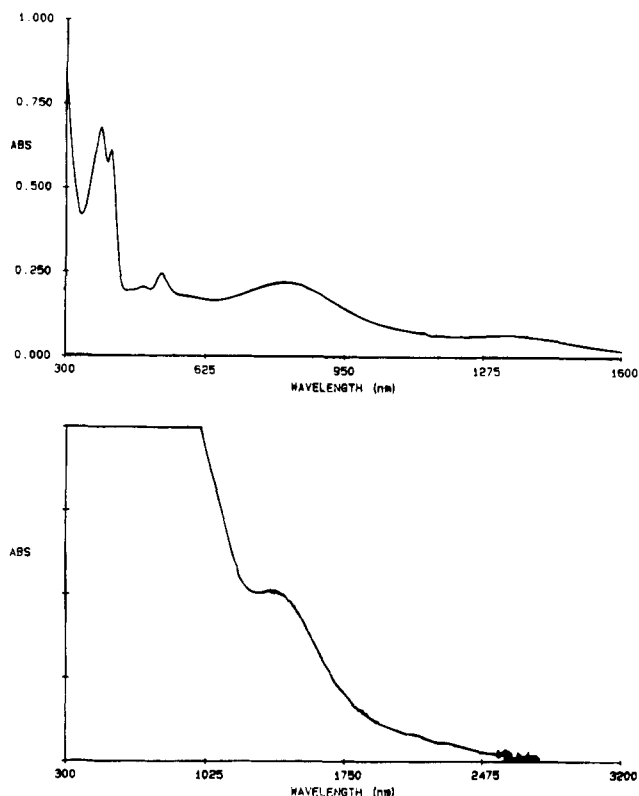


Figure 5. Electronic spectra of  $\text{Cu}(\text{PhenoxSQ})_2$  in toluene solution (top) and in the solid state (bottom) to show the low-energy transition at 1290 nm.

planarity for the molecule. Magnetic measurements over the temperature range between 77 and 470 K have provided values for magnetic moment that increase from  $1.87 \mu_B$  at the low-temperature limit to  $2.88 \mu_B$ . Temperature dependence was modeled with  $J_{\text{SQ-SQ}}$  of  $-179 \text{ cm}^{-1}$  and  $J_{\text{Cu-SQ}}$  of  $100 \text{ cm}^{-1}$ . Changes in the magnetic moment of  $\text{Cu}(\text{PhenoxSQ})_2$  follow the temperature dependence of  $\text{Cu}(3,6\text{-DBSQ})_2$ , but the simple model consisting of antiferromagnetic SQ-SQ exchange and ferromagnetic Cu-SQ coupling does not apply because of the change in orientation of magnetic axes. Attempts at modeling the magnetic behavior of  $\text{Cu}(\text{PhenoxSQ})_2$  have shown that two opposing coupling constants may be used to give a reasonable fit, but their magnitudes are highly correlated and the coupling scheme is unclear. Misalignment of magnetic coordinates associated with the irregular tetrahedral structure of Cu-

(14) Fox, G. A.; Pierpont, C. G. *Inorg. Chem.* **1992**, *31*, 3718.

(15) Abakumov, G. A.; Cherkasov, V. K.; Bubnov, M. P.; Ellert, O. G.; Rakitin, U. V.; Zakharov, L. N.; Struchkov, Y. T.; Saf'yanov, U. N. *Izv. Akad. Nauk, Ser. Khim.* **1992**, 2315.

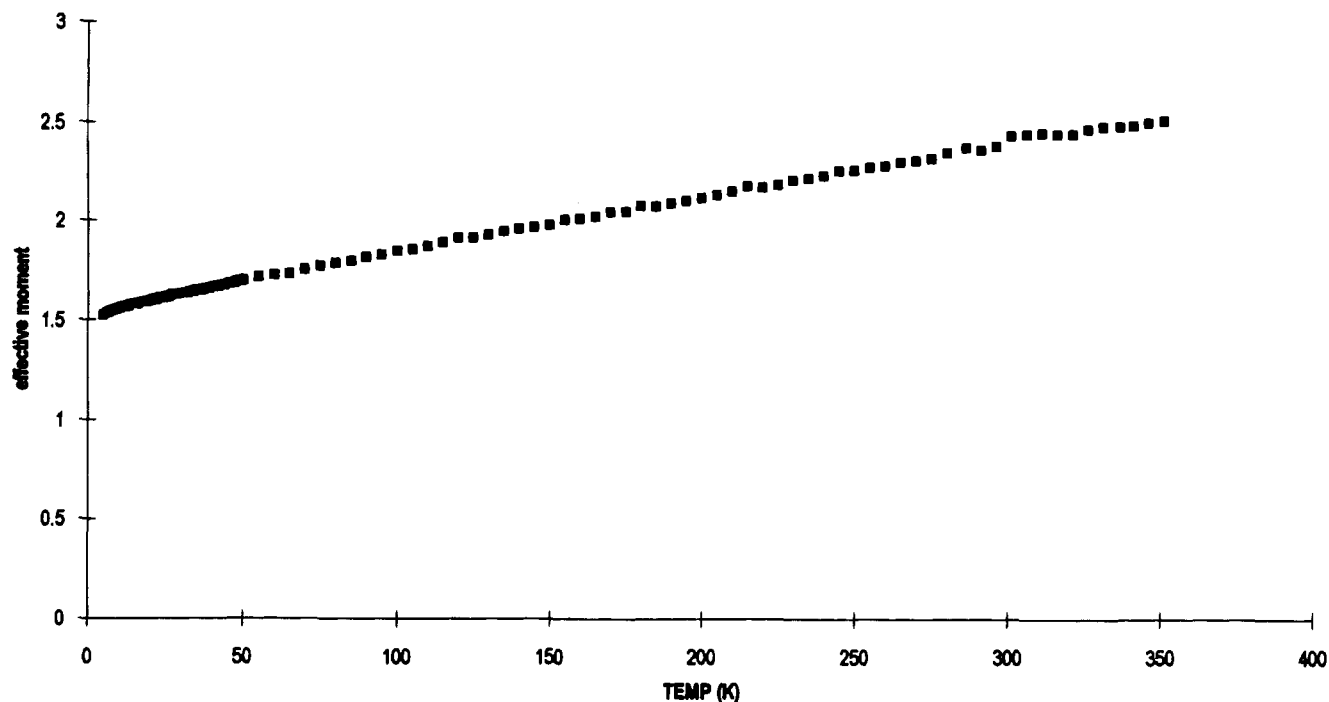


Figure 6. Temperature-dependent changes in the magnetic moment of  $\text{Cu}(\text{PhenoxSQ})_2$ .

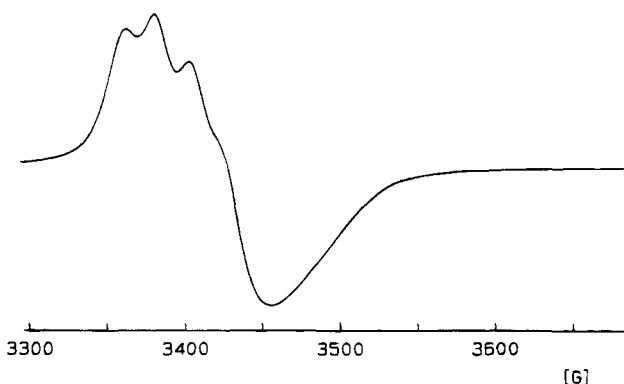


Figure 7. EPR spectrum of  $\text{Cu}(\text{PhenoxSQ})_2$  recorded in a toluene glass at 77 K at a frequency of 9.454 GHz.

$(\text{PhenoxSQ})_2$  results in a shift in magnetic ground state relative to the planar model, and this is particularly clear from its EPR spectrum. The axial anisotropic EPR spectrum of  $\text{Cu}(3,6\text{-DBSQ})_2$  consists of  $g$  components of  $g_{\perp} = 2.00$  and  $g_{\parallel} = 2.23$ , with  $A_{\parallel}(\text{Cu}) = 20$  G, and on this basis it was concluded that the ground state spin was metal-based. While the anisotropy of the spectrum reflects a spin-orbit coupling contribution that may be in accord with this conclusion, the hyperfine coupling on  $g_{\parallel}$  is significantly less than would be expected for a  $\text{Cu}^{\text{II}}\text{O}_4$  complex.<sup>16</sup> The EPR spectrum of  $\text{Cu}(\text{PhenoxSQ})_2$  is even more unusual. The anisotropic spectrum obtained in a toluene glass at 77 K is shown in Figure 7. It consists of two components with weak Cu hyperfine coupling of 25 G on the low-field component. What is most unusual is that the low-field component is centered about a  $g$  value of 1.996 and the high-field component about  $g = 1.973$ . The absence of a positive spin-orbit coupling contribution to the anisotropic  $g$  tensor points strongly to a ligand-based spin system. Complexes that contain multiple radical ligands coupled to give a radical-based  $S = 1/2$  ground state are rare. The  $\text{V}^{\text{III}}(\text{SQ})_3$  complexes have ligand-based spins due to strong coupling with the metal ion,<sup>17</sup> and  $\text{Co}^{\text{III}}(3,6\text{-DBSQ})_3$  has a  $S = 1/2$  ground state due to

intrradical antiferromagnetic exchange.<sup>18</sup> The anisotropic EPR spectrum of this complex closely resembles that of  $\text{Cu}(\text{PhenoxSQ})_2$  as a two-component spectrum centered about a  $g$  value of 1.998 with  $^{59}\text{Co}$  ( $I = 7/2$ ) coupling of 22.6 G on the low-field component. In fact,  $\text{Co}(3,6\text{-DBSQ})_2$  and  $\text{Cu}(\text{PhenoxSQ})_2$  resemble one another in one other unique respect. In solution at room temperature, a temperature where magnetic measurements on both complexes in the solid state give values that approach the  $3.0 \mu_{\text{B}}$  value for three noninteracting spin centers, clear NMR spectra may be observed for the ligand *tert*-butyl substituents. For  $\text{Co}(3,6\text{-DBSQ})_3$ , and also  $\text{Ga}(3,6\text{-DBSQ})_3$  with radical ligands that are ferromagnetically coupled, a single, sharp *tert*-butyl resonance may be observed near 2.00 ppm at 35 °C.<sup>18</sup> Spectra recorded on  $\text{Cu}(\text{PhenoxSQ})_2$  in toluene- $d_8$  at temperatures where no solution EPR spectrum is observed are shown in Figure 8. Four sharp resonances are observed for the *tert*-butyl substituents of the equivalent PhenoxSQ ligands at room temperature at 0.91, 0.97, 1.65, and 2.53 ppm. With decreasing temperature, the downfield resonance shifts further downfield to 4.35 ppm at 193 K and the upfield resonances shift upfield to 0.54 and 1.40 ppm. For comparison, *tert*-butyl resonances appear at 1.201, 1.306, 1.420, and 1.497 ppm for  $\text{Ni}(\text{PhenoxSQ})_2$ , at 2.006, 1.451, 1.333, and 0.810 ppm for  $\text{cis-Ru}(\text{CO})_2(\text{PhenoxSQ})_2$ , and at 1.505, 1.453, 1.319, and 1.308 ppm for free PhenoxBQ.<sup>2,10</sup> The appearance of proton resonances for strongly paramagnetic radical-ligand complexes has precedence in our experience only for members of the  $\text{M}(3,6\text{-DBSQ})_3$  ( $\text{M} = \text{Co}, \text{Ga}, \text{Al}$ ) series.<sup>18</sup>

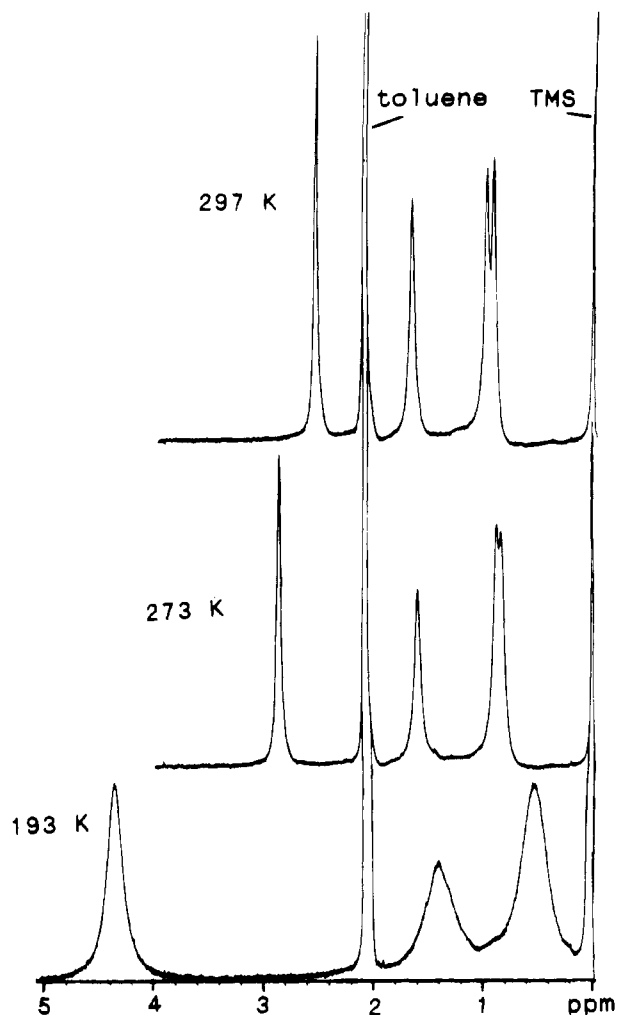
## Discussion

The copper complexes of the PhenoxSQ ligand undergo ligand-based redox reactions without observable electrochemical activity at the metal. Related complexes of copper containing the 3,5- and 3,6-DBSQ ligands undergo similar reactions, but

(17) (a) Cass, M. E.; Greene, D. L.; Buchanan, R. M.; Pierpont, C. G. *J. Am. Chem. Soc.* **1983**, *105*, 2680. (b) Cass, M. E.; Gordon, N. R.; Pierpont, C. G. *Inorg. Chem.* **1986**, *25*, 3962.

(18) Lange, C. W.; Conklin, B. J.; Pierpont, C. G. *Inorg. Chem.* **1994**, *33*, 1276.

(16) Peisach, J.; Blumberg, W. E. *Arch. Biochem. Biophys.* **1974**, *165*, 691.



**Figure 8.**  $^1\text{H}$  NMR spectra of  $\text{Cu}(\text{PhenoxSQ})_2$  in  $\text{toluene-}d_8$  showing the temperature dependence of the *tert*-butyl proton resonances.

at potentials shifted positively by roughly 0.5 V. Copper complexes formed with the fully reduced amidophenolate form of the PhenoxBQ ligand, PhenoxCat, would be strong reducing

agents. This conclusion may be extended to copper complexes formed by chelation with the tetrahydropterin cofactors of the copper-containing *Chromobacterium violaceum* phenylalanine hydroxylase<sup>6</sup> and may be relevant to observations on potential aminoquinone–copper interactions in the amine oxidase enzymes.<sup>19</sup> The substituents and ring structure of PhenoxSQ do not permit coplanar coordination for  $\text{Cu}(\text{PhenoxSQ})_2$  and  $\text{Ni}(\text{PhenoxSQ})_2$ , and as a consequence the complexes have distorted tetrahedral structures. Even with distortion, the ligand-based spin of  $\text{Cu}(\text{PhenoxSQ})_2$  shows that the magnetic properties of the complex are those of a tetrahedral, rather than planar, molecule. In this case, EPR provides clear insight into the structure. Both  $\text{Cu}(\text{PhenoxSQ})_2$  and  $\text{Co}(3,6\text{-DBSQ})_3$ , as complexes where ligand spin may be located on one of two or three radical centers, are molecules that may show the effects of radical spin frustration. In the absence of proton hyperfine coupling, it is not possible to determine whether the unpaired spin is contained on one ligand, whether it is moving rapidly over equivalent ligands on some finite time scale or whether it is delocalized.<sup>20</sup> In fact, the absence of proton hyperfine coupling may be the result of a dynamic process, and the anomalous negative shift in *g* tensor, the consequence of rapid electron transfer between nominally equivalent radical sites.

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**Supplementary Material 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  $\text{Cu}(\text{PPh}_3)_2(\text{PhenoxSQ})$  and  $\text{Cu}(\text{PhenoxSQ})_2$  (28 pages). Ordering information is given on any current masthead page.

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(19) Mure, M.; Klinman, J. P. *J. Am. Chem. Soc.* **1993**, *115*, 7117.

(20) Liberko, C. A.; Miller, L. L.; Katz, T. J.; Liu, L. *J. Am. Chem. Soc.* **1993**, *115*, 2478.