

Iminoquinone Complexes of Iron and Nickel. Structural, Magnetic, and Electrochemical Properties of Complexes Containing the Phenoxazinolate Semiquinone Radical

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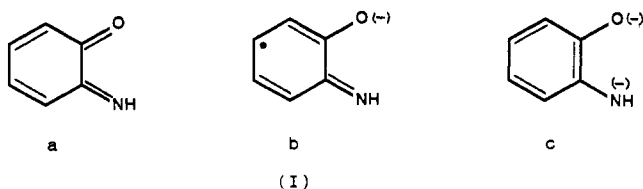
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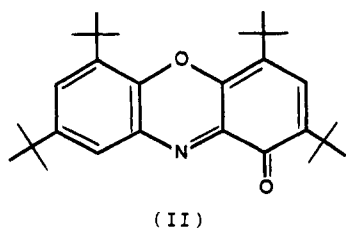
Complexes have been formed by the coordination of 2,4,6,8-tetra-*tert*-butylphenoxazin-1-one (PhenoxBQ) with iron(III) and nickel(II). Addition of PhenoxBQ to a solution of anhydrous FeCl₃ gives [Fe(PhenoxBQ)₂Cl₂](FeCl₄). Reduction of this complex occurs at the iminoquinone ligands to give Fe(PhenoxSQ)₂Cl. Crystallographic characterization (triclinic, $P\bar{1}$, $a = 14.151(2)$ Å, $b = 15.170(2)$ Å, $c = 16.326(2)$ Å, $\alpha = 80.73(1)^\circ$, $\beta = 77.28(1)^\circ$, $\gamma = 64.54(1)^\circ$, $V = 3077.9(7)$ Å³, $Z = 2$, $R = 0.063$) has shown that the complex molecule is trigonal bipyramidal in structure with the chloro ligand bonded in an equatorial site. Radical iminosemiquinone ligands couple antiferromagnetically with the paramagnetic metal to give a magnetic moment of 3.78 μ_B for the molecule at room temperature. Cyclic voltammograms show that the complex undergoes two oxidations and two reductions within the potential range ± 1.2 V (vs NHE) that are iminoquinone ligand based and a third reduction at the metal at -1.427 V. Addition of PhenoxBQ to Ni(NO₃)₂ gives [Ni(PhenoxBQ)₂(NO₃)](NO₃). Structural characterization (triclinic, $P\bar{1}$, $a = 12.752(2)$ Å, $b = 13.700(2)$ Å, $c = 20.676(3)$ Å, $\alpha = 102.03(1)^\circ$, $\beta = 98.70(1)^\circ$, $\gamma = 114.02(1)^\circ$, $V = 3112.4(8)$ Å³, $Z = 2$, $R = 0.072$) has shown that the complex cation is octahedral with the nitrate ligand chelated through two oxygen atoms. Reduction of this complex also occurs at the iminoquinone ligands to give Ni(PhenoxSQ)₂. This molecule is tetrahedral in structure (monoclinic, $P2_1/c$, $a = 26.029(5)$ Å, $b = 17.604(6)$ Å, $c = 12.118(2)$ Å, $\beta = 98.23(1)^\circ$, $V = 5496(2)$ Å³, $Z = 4$, $R = 0.066$) and diamagnetic, due to strong antiferromagnetic coupling between the radical ligands and the metal ion. Electrochemical characterization has shown that the complex undergoes two oxidations and two reductions that are ligand-based. Coordination of PhenoxBQ results in shifts in $\nu(\text{CO})$ and $\nu(\text{CN})$ to lower energy with further low-energy shifts upon reduction to PhenoxSQ for complexes of both metals. Lengths of the C–O and C–N bonds within the chelate ring are longer than those of free PhenoxBQ and increase further upon reduction. Reduction couples of the PhenoxBQ and PhenoxSQ ligands are shifted positively by nearly 2.0 V upon coordination, and radical iminosemiquinone ligands couple antiferromagnetically with the paramagnetic metal ions.

Introduction

The coordination chemistry of the quinone ligands in their various electronic forms has been rich and unusual.¹ It has been of interest to extend these investigations to the *o*-iminoquinones, where iminobenzoquinone (Ia), iminosemiquinone (Ib), and

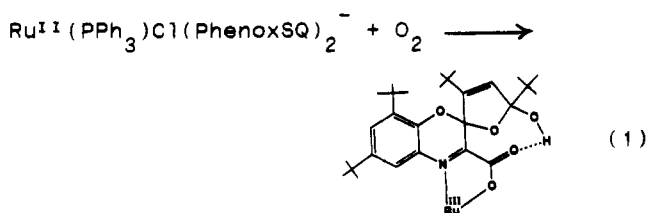


amidophenolate (Ic) forms of the ligand may serve as nitrogen–oxygen analogs of the more common benzoquinone, semiquinone, and catecholate ligands. Synthetic difficulties have inhibited the study of iminoquinone complexes, although Lever has recently reported spectroscopic studies on a series of ruthenium compounds.² The *tert*-butyl-substituted phenoxazinone (II, Phe-



noxBQ) may be conveniently prepared,³ and it offers the possibility

for studies on iminoquinone complexes of metals of the first transition series. Earlier research on ruthenium complexes of this ligand revealed a surprising oxidation reaction that resulted in oxidative cleavage of the iminoquinone ring (eq 1).⁴ This

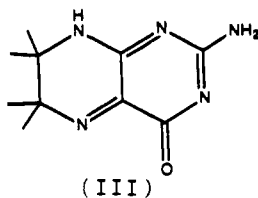


reaction may be related to synthetic catechol oxidation reactions that have been intensively studied with a variety of metal ions.^{1b} Iron complexes have been of particular interest since the metal is a common component in many synthetic oxidation systems and it is often associated with the function of metalloenzymes that carry out biological oxidation reactions. A growing class of predominantly iron-containing metalloenzymes use reduced pterin cofactors to bind and activate dioxygen for subsequent substrate hydroxylation. These include tryptophan hydroxylase, tyrosine hydroxylase, and, most notably, phenylalanine hydroxylase (PAH).⁵ While evidence for a direct interaction between iron and the reduced pterin cofactor is lacking, characterization on a bacterial form of PAH that contains copper has demonstrated an association between the quinoid region of the pterin and the

* Abstract published in *Advance ACS Abstracts*, January 1, 1994.
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 (4) (a) Bhattacharya, S.; Boone, S. R.; Pierpont, C. G. *J. Am. Chem. Soc.* **1990**, *112*, 4561. (b) Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.* **1992**, *31*, 2020.

metal.⁶ This observation prompted studies on copper complexes of the aromatic pterins.⁷ Electrochemical characterization on PhenoxBQ has shown that reduction potentials of the iminoquinone are comparable to the reduction potentials of the quinonoid dihydropterins (III), although pH-dependent tauto-



meric rearrangements involving the heterocyclic ring complicate the electrochemistry (and the chemistry) of these molecules in their various states of reduction. The PhenoxBQ ligand in its electronic forms may serve as a simple redox-active functional model for coordinated dihydrobiopterins.^{4b,8} This has provided a specific interest in the synthesis and characterization of iron complexes of the PhenoxBQ ligand. These studies have been coupled with work on related complexes of nickel enabling identification of separate metal- and ligand-based redox processes.

Experimental Section

Materials. 2,4,6,8-Tetra-*tert*-butylphenoxazin-1-one (PhenoxBQ) was prepared according to a literature procedure.³

[Fe(PhenoxBQ)₂Cl₂](FeCl₄). Anhydrous FeCl₃ (25.6 mg, 0.158 mmol) and PhenoxBQ (200 mg, 0.474 mmol) were dissolved in 40 mL of ethanol, and the solution was stirred for 3 h. The solvent was then evaporated under reduced pressure, and the residue was washed free of excess PhenoxBQ with hexane. The complex was recrystallized from a dichloromethane/hexane solution to give 120 mg of [Fe(PhenoxBQ)₂Cl₂](FeCl₄) as thin yellow-green plates. Analytical data indicated that the crystals formed as hexane solvates, and this was confirmed by a structure determination.

Fe(PhenoxSQ)₂Cl. [Fe(PhenoxBQ)₂Cl₂](FeCl₄) (80 mg, 0.064 mmol) and cobaltocene (24.2 mg, 0.128 mmol) were combined in 40 mL of benzene under N₂. The solution became dark brown, and yellow-orange salts of CoCp₂⁺ precipitated. The benzene was removed by evaporation, and the neutral complex product was extracted from the residue with hexane. Recrystallization from hexane gave 30 mg of Fe(PhenoxSQ)₂Cl·C₆H₁₄ as green-brown crystals.

[Ni(PhenoxBQ)₂(NO₃)](NO₃). Ni(NO₃)₂·6H₂O (69 mg, 0.237 mmol) and PhenoxBQ (200 mg, 0.474 mmol) were dissolved in 35 mL of ethanol, and the solution was stirred for 3 h. The solvent was evaporated under reduced pressure, and the residue was washed with hexane. Recrystallization of the residue from dichloromethane gave 174 mg of [Ni(PhenoxBQ)₂(NO₃)](NO₃) as green crystals of the dichloromethane solvate.

Ni(PhenoxSQ)₂. [Ni(PhenoxBQ)₂(NO₃)](NO₃) (75 mg, 0.073 mmol) and cobaltocene (27.7 mg, 0.146 mmol) were combined under N₂, and 25 mL of benzene was distilled into the flask. The mixture immediately turned dark red. The benzene was removed by evaporation, and the

Table 1. Crystallographic Data for Fe(PhenoxSQ)₂Cl, [Ni(PhenoxBQ)₂(NO₃)](NO₃), and Ni(PhenoxSQ)₂^a

	Fe(PhenoxSQ) ₂ Cl	[Ni(PhenoxBQ) ₂ (NO ₃)](NO ₃)	Ni(PhenoxSQ) ₂
fw	1020.6	1175.8	901.9
color	green-brown	green	red
cryst system	triclinic	triclinic	monoclinic
space group	P $\bar{1}$	P $\bar{1}$	P ₂ /c
a, Å	14.151(2)	12.752(2)	26.029(5)
b, Å	15.170(2)	13.700(2)	17.604(6)
c, Å	16.326(2)	20.676(3)	12.118(2)
α, deg	80.73(1)	102.03(1)	90.00
β, deg	77.28(1)	98.70(1)	98.23(1)
γ, deg	64.54(1)	114.02(1)	90.00
V, Å ³	3077.9(7)	3112.4(8)	5496(2)
Z	2	2	4
D _{calcd} , g cm ⁻³	1.051	1.255	1.090
μ, mm ⁻¹	0.362	0.537	0.394
R, R _w	0.063, 0.084	0.072, 0.090	0.066, 0.072
GOF	1.69	2.02	1.43

^a Radiation, Mo Kα (0.710 73 Å); temperature, 295–298 K.

complex was extracted from the solid residue with hexane. Recrystallization from dry hexane gave 55 mg of Ni(PhenoxSQ)₂ as dark red crystals.

Physical Measurements. Electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. Infrared spectra were obtained on an IBM IR/30 FTIR spectrometer with samples prepared as KBr pellets. ¹H 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 platinum disk working electrode and a platinum wire counter electrode were used. A Ag/Ag⁺ reference electrode was used that consisted of a CH₃CN solution of AgPF₆ in contact with a silver wire placed in glass tubing with a Vycor frit at one end to allow ion transport. Tetrabutylammonium hexafluorophosphate (TBHP) was used as the supporting electrolyte, and the ferrocene/ferrocenium couple was used as an internal standard. Potentials were converted to the NHE reference by assuming that the Fe/Fe⁺ couple occurs at +0.400 V vs NHE.

Crystallographic Structure Determinations. [Fe(PhenoxBQ)₂Cl₂](FeCl₄)·C₆H₁₄. Crystals of the complex form as thin yellow-green plates with a tendency toward twinning along the thin axis of the plate. A crystal of dimensions 0.43 × 0.36 × 0.003 mm, the largest single crystal obtained, was mounted and aligned on the diffractometer. The crystal was monoclinic, space group P₂/c, in a unit cell of dimensions a = 19.871(9) Å, b = 18.483(8) Å, c = 18.185(7) Å, and β = 103.32(3)°. Two related quadrants of data were collected within the 2θ range between 3.0 and 45.0° using Mo Kα radiation. Of 6097 unique, averaged reflections measured, only 2356 were observed at F > 4.0σ(F). Iron and chlorine atoms were located using the Patterson method; other atoms were located on difference Fourier maps. Methyl carbon atoms of the *tert*-butyl groups were found to suffer from rotational disorder, and atoms of the hexane solvate were disordered. The structure was refined isotropically to R = 0.15 with all non-hydrogen atoms, and the structure determination was terminated due to the low reflection-to-parameter ratio. Attempts at crystallization from other solvents have failed to provide samples that would be more satisfactory for structural characterization.

Fe(PhenoxSQ)₂Cl·C₆H₁₄. Crystals obtained by recrystallization from CH₂Cl₂/hexane solution form as dark brown parallelepipeds. 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 θ-2θ scans on a Siemens P3 diffractometer within the angular range 3.0–50.0°. The structure was solved using direct methods. One end carbon atom of the hexane solvate was found to be disordered between two locations. Final cycles of refinement, including fixed contributions for the hydrogen atoms, converged with discrepancy indices of R = 0.063 and R_w = 0.084. Tables containing atom positions, anisotropic displacement parameters, hydrogen atom positions, bond lengths, and bond angles are available as supplementary material.

[Ni(PhenoxBQ)₂(NO₃)](NO₃)·2CH₂Cl₂. Crystals obtained by slow evaporation of a CH₂Cl₂ solution form as dark green plates. 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 θ-2θ scans on a Siemens P3 diffractometer within the

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Table 2. Spectral Bands for PhenoxBQ and Complexes of Iron and Nickel Recorded in Dichloromethane Solution

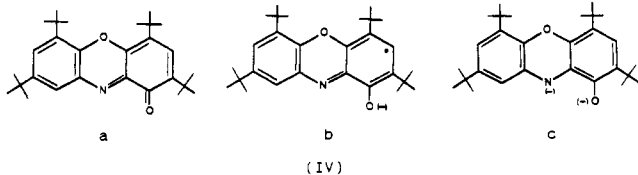
	λ_{\max} , nm (ϵ , M ⁻¹ cm ⁻¹)	$\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$, cm ⁻¹
PhenoxBQ	362 (8100), 616 (4400)	1643, 1582
[Fe(PhenoxBQ) ₂ Cl ₂] ⁺	328 sh (17 400), 434 (19 400), 834 (6300)	1613, 1551
Fe(PhenoxSQ) ₂ Cl	374 (12 100), 498 (8800), 796 (6400)	1534, 1480
[Ni(PhenoxBQ) ₂ (NO ₃) ₂] ⁺	393 (15 700), 417 (8050), 516 (3050), 810 (2670)	1617, 1577
Ni(PhenoxSQ) ₂	367 (16 300), 379 sh (15 350), 455 (10 350), 519 (13 800), 809 (5150)	1530, 1483

angular range 3.0–45.0°. The structure was solved using Patterson methods. Final cycles of refinement, including fixed contributions for the hydrogen atoms, converged with discrepancy indices of $R = 0.072$ and $R_w = 0.090$. Tables containing atom positions, anisotropic displacement parameters, hydrogen atom positions, bond lengths, and bond angles are available as supplementary material.

[Ni(PhenoxSQ)₂. Crystals obtained by slow evaporation of a hexane solution form as dark red plates. 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 θ - 2θ scans on a Siemens P3 diffractometer within the angular range 3.0–45.0°. The space group was determined to be $P2_1/c$, and the structure was solved using Patterson methods. Other structure determinations on complexes containing PhenoxSQ ligands have shown that the ligand is often folded at the central nitrogen and oxygen atoms.^{4b} In this structure determination a fold of approximately 16° disorders carbon atoms C3, C4, and C5 and the associated *tert*-butyl group between two fixed locations with approximately equal occupancies. Final cycles of refinement, including fixed contributions for the hydrogen atoms, converged with discrepancy indices of $R = 0.066$ and $R_w = 0.072$. Tables containing atom positions, anisotropic displacement parameters, hydrogen atom positions, bond lengths, and bond angles are available as supplementary material.

Experimental Results

The absence of studies on the coordination chemistry of iminoquinone ligands has prompted our investigation on complexes of the PhenoxQ ligand in its three electronic forms (IV). The



oxidized *o*-imino benzoquinone (PhenoxBQ, IVa) may be expected to form more stable complexes than the corresponding benzoquinones due to the presence of the imino nitrogen donor atom. The first reduction of PhenoxBQ lies at a potential that is slightly more negative than that of 3,5-di-*tert*-butyl-1,2-benzoquinone (3,5-DBBQ), and it is not unreasonable to expect that PhenoxSQ will have a coordination chemistry similar to that of 3,5-DBSQ. The second reduction of PhenoxBQ appears at a potential that is 0.5 V more negative than the 3,5-DBSQ/3,5-DBCat couple and the fully reduced amidophenolate form of the ligand, PhenoxCat, may form complexes that are more reductive and air-sensitive than the corresponding catecholate analogs. In our present investigation complexes have been formed initially with PhenoxBQ, with more reduced forms obtained by chemical and electrochemical reduction.

[Fe(PhenoxBQ)₂Cl₂](FeCl₄). The addition of a slight excess of PhenoxBQ to an ethanol solution of anhydrous FeCl₃ resulted in the formation of yellow-green [Fe(PhenoxBQ)₂Cl₂](FeCl₄). Recrystallization of the complex from a hexane/dichloromethane mixture gave thin crystalline plates of the complex as a hexane solvate. One of the largest crystals was investigated crystallographically. However, the small volume of the crystal together with an unstable and highly disordered solvate structure gave intensity data of marginal quality, not sufficient for a high-quality structure determination. Gross features of the complex cation, anion, and solvate were apparent, providing information on the compound that we had been unable to obtain by other analytical

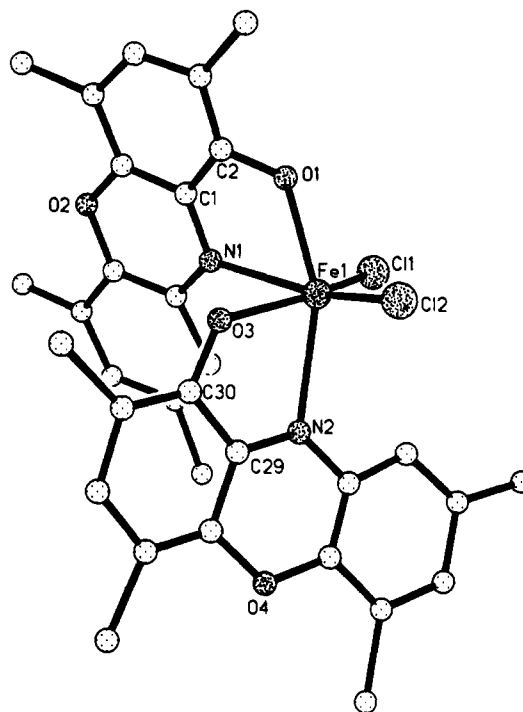
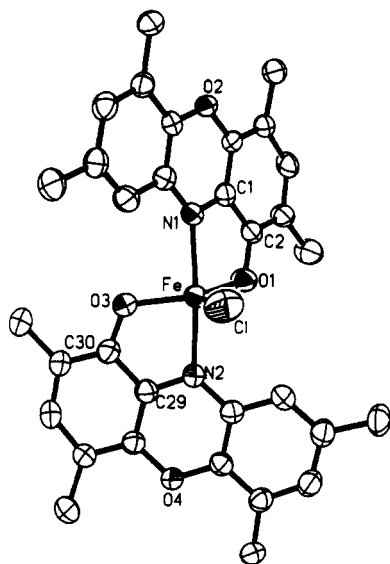


Figure 1. View of the [Fe(PhenoxBQ)₂Cl₂]⁺ cation. Methyl carbon atoms of the *tert*-butyl groups have been omitted.

means. A view of the cation is shown in Figure 1. An unusual feature of this ionic compound is its solubility in nonpolar solvents (i.e. hexane, benzene) leading to initial assumptions that the complex was neutral in charge. This is presumably due to a strong cation–anion interaction that is not apparent in the crystal structure. Infrared spectra on the complex show strong $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$ stretching vibrations at 1613 and 1551 cm⁻¹ (Table 2). Related vibrations for the free PhenoxBQ ligand occur at 1643 and 1582 cm⁻¹. Free PhenoxBQ is deep blue in color due to a visible transition at 616 nm (4400 M⁻¹ cm⁻¹). Complexation with Fe³⁺ in [Fe(PhenoxBQ)₂Cl₂]⁺ results in a dramatic color change due to an intense transition at 434 nm (19 400 M⁻¹ cm⁻¹) and a band of lower intensity at 834 nm (6320 M⁻¹ cm⁻¹). Both the PhenoxBQ ligands and the Fe(III) center may be subject to reduction, and the products of chemical reduction reactions are described below.

Fe(PhenoxSQ)₂Cl. The solubility of [Fe(PhenoxBQ)₂Cl₂](FeCl₄) in benzene provided a convenient synthetic route to reduced forms of the complex. Treatment of the benzene solution with 2 equiv of cobaltocene resulted in separation of cobaltocenium salts, with the reduced product remaining in the solution. Isolation and crystallographic characterization of the complex indicated that it is the five-coordinate Fe(PhenoxSQ)₂Cl molecule shown in Figure 2. The neutral iron complex is trigonal bipyramidal in structure with axial nitrogen donors and the chloro ligand bonded in an equatorial site. Selected bond distances and angles are listed in Table 3. Features of the PhenoxSQ ligands may be viewed as characteristic of coordinated iminosemiquinones. The C–O and C–N lengths within the chelate ring are longer than values reported for PhenoxBQ (Table 4) but shorter than single bond lengths at other positions in the ligand. Carbon–oxygen lengths within the chelate ring average 1.315(6) Å, slightly longer

Figure 2. View of $\text{Fe}(\text{PhenoxSQ})_2\text{Cl}$.Table 3. Selected Bond Lengths and Angles for $\text{Fe}(\text{PhenoxSQ})_2\text{Cl}$

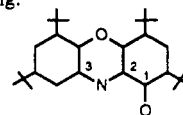
Bond Lengths (Å)			
Iron			
Fe-O1	1.928(5)	Fe-N2	2.079(4)
Fe-O3	1.920(4)	Fe-Cl	2.240(2)
Fe-N1	2.086(4)		
PhenoxSQ-1			
O1-C2	1.314(6)	C3-C4	1.397(7)
N1-C1	1.345(8)	C4-C5	1.415(9)
N1-C7	1.385(8)	C5-C6	1.388(8)
C1-C2	1.431(9)	C1-C6	1.412(7)
C2-C3	1.382(9)	C6-O2	1.384(7)
PhenoxSQ-2			
O3-C30	1.316(6)	C31-C32	1.394(7)
N2-C29	1.340(7)	C32-C33	1.419(9)
N2-C35	1.384(8)	C33-C34	1.374(8)
C29-C30	1.441(9)	C29-C34	1.417(6)
C30-C31	1.387(8)	C34-O4	1.383(7)
Bond Angles (deg)			
Iron			
Cl-Fe-N1	96.4(1)	Cl-Fe-O1	118.9(1)
N1-Fe-O1	79.4(2)	Cl-Fe-N2	96.3(1)
N1-Fe-N2	167.4(2)	O1-Fe-N2	94.4(2)
Cl-Fe-O3	121.4(1)	N1-Fe-O3	93.9(2)
O1-Fe-O3	119.6(2)	N2-Fe-O3	79.5(2)
PhenoxSQ-1			
Fe-O1-C2	117.8(4)	N1-C1-C2	114.5(4)
O1-C2-C1	116.1(5)	Fe-N1-C1	112.0(4)
PhenoxSQ-2			
Fe-O3-C30	118.3(4)	N2-C29-C30	114.7(4)
O3-C30-C29	115.1(5)	Fe-N2-C29	112.1(4)

than a typical coordinated semiquinone value and considerably shorter than the C-O length of 1.387(7) Å to the ring phenoxazine oxygen atoms, O2 and O4. The degree to which the iminosemiquinone region of the ligand is conjugated with the aromatic region of the tricyclic phenoxazine is of interest with respect to the suitability of the ligand as a model for the quinonoid dihydropterins. Carbon-oxygen lengths to the ether oxygen are of reasonable single-bond values, and the two C-N lengths to the coordinated nitrogen atoms differ significantly. Partial multiple character of C-N lengths within the chelate ring results in an average length of 1.343(7) Å, which may be compared with the 1.305(6) Å value of PhenoxBQ. Carbon-nitrogen lengths outside the chelate ring of $\text{Fe}(\text{PhenoxSQ})_2\text{Cl}$ are both 1.384(7) Å, no different than the value for PhenoxBQ. These structural features

Table 4. Characteristic Bond Lengths (Å) of PhenoxBQ and PhenoxSQ Ligands

	O-C1 ^a	N-C2	C1-C2	N-C3
PhenoxBQ				
PhenoxBQ ^b	1.239(7)	1.305(6)	1.470(6)	1.375(5)
$[\text{Ni}(\text{PhenoxBQ})_2(\text{NO}_3)]^+$	1.28(1)	1.32(1)	1.46(1)	1.38(1)
PhenoxSQ				
$\text{Fe}(\text{PhenoxSQ})_2\text{Cl}$	1.315(6)	1.343(7)	1.436(9)	1.385(8)
$\text{Ni}(\text{PhenoxSQ})_2$	1.29(1)	1.34(1)	1.42(1)	1.38(1)
$\text{Ru}(\text{PPh}_3)_2\text{Cl}_2(\text{PhenoxSQ})^b$	1.300(4)	1.363(4)	1.442(5)	1.417(4)
$\text{Ru}(\text{PPh}_3)_2\text{Cl}(\text{PhenoxSQ})_2^b$	1.316(7)	1.364(7)	1.427(8)	1.389(7)

^a Atoms C1 and C2 are included in the chelate ring; the N-C3 bond is outside the chelate ring:



^b Reference 4b.

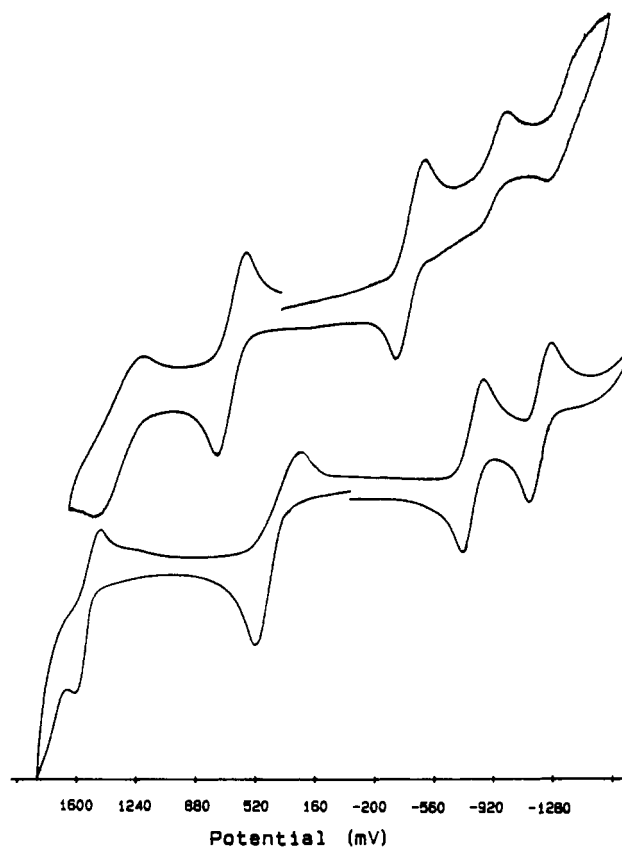


Figure 3. Cyclic voltammograms showing the redox series of (a) $\text{Fe}(\text{PhenoxSQ})_2\text{Cl}$ and (b) $\text{Ni}(\text{PhenoxSQ})_2$. Dichloromethane was used as the solvent, scan rates were 100 mV/s, and potentials were referenced to NHE.

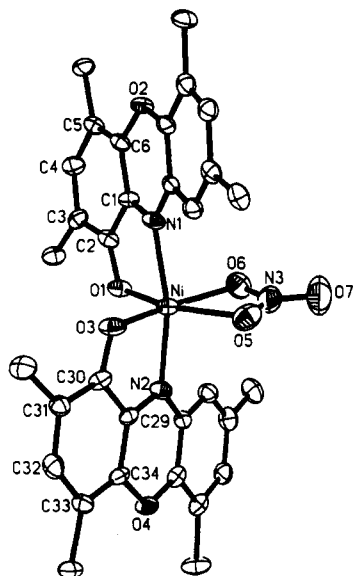
show that within the limits of crystallographic resolution there is little conjugation between the iminoquinone region of the ligand and the adjacent aromatic ring.

Reduction of the ligands of $[\text{Fe}(\text{PhenoxBQ})_2\text{Cl}_2]^+$ results in a low-energy shift in $\nu(\text{C}-\text{O})$ and $\nu(\text{C}-\text{N})$ to 1534 and 1480 cm^{-1} (Table 2). Crystals of $\text{Fe}(\text{PhenoxSQ})_2\text{Cl}$ are dark brown in color due to two transitions in the visible region at 498 (8800 $\text{M}^{-1}\text{cm}^{-1}$) and 796 nm (6400 $\text{M}^{-1}\text{cm}^{-1}$). Cyclic voltammograms on the complex show four reversible or quasireversible couples that are ligand-based oxidations and reductions (Figure 3). Oxidations that correspond to PhenoxBQ/PhenoxSQ⁻ couples appear at +1.203 and +0.515 V (vs NHE), and PhenoxSQ⁻/PhenoxCat²⁻ reductions of the ligands appear at -0.580 and -1.089 V (Table 5). An additional reduction appears at -1.427 V, which likely corresponds to reduction of the metal to Fe(II). Magnetic coupling between the paramagnetic Fe(III) center and the radical

Table 5. Electrochemical Potentials (vs NHE) for PhenoxBQ, Fe(PhenoxSQ)₂Cl, and Ni(PhenoxSQ)₂

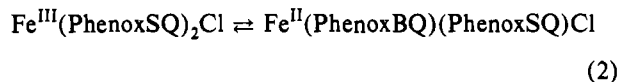
compd	<i>E</i> _{1/2} , V vs NHE (ΔE , mV) ^a				
	OxII	OxI	RedI	RedII	RedIII
PhenoxBQ			-0.849 (98)	-1.747 (<i>E</i> _{pc})	
Fe(PhenoxSQ) ₂ Cl	1.203 (278)	0.515 (175)	-0.580 (183)	-1.089 (<i>E</i> _{pc})	-1.427 (<i>E</i> _{pa})
Ni(PhenoxSQ) ₂	1.524 (147)	0.432 (286)	-0.790 (126)	-1.211 (132)	

^a In dichloromethane (0.1 M TBAP) at 23 °C. *E*_{1/2} = half-wave potential; ΔE = peak separation between anodic and cathodic peaks of CV.


Figure 4. View of the [Ni(PhenoxBQ)₂(NO₃)]⁺ cation.

iminosemiquinone ligands is strong and antiferromagnetic. The magnetic moment of Fe(PhenoxSQ)₂Cl is 3.78 μ_B at 298 K and remains constant to 77 K. Below 77 K there is a gradual drop to 2.89 μ_B at 5.0 K due, presumably, to intermolecular interactions. The room-temperature value is close to the moment expected for a *S* = 3/2 spin ground state that would arise from strong antiferromagnetic exchange between the two *S* = 1/2 radical ligands and the *S* = 5/2 metal ion.

PhenoxSQ oxidation observed for reduced Ru(PPh₃)Cl-(PhenoxSQ)₂ (eq 1) may also occur with iron, and the vacant coordination site of Fe(PhenoxSQ)₂Cl offers a possibility for small-molecule coordination. The formation of Fe(NO)(PhenoxSQ)₂Cl was investigated by placing a toluene solution of the parent complex under an atmosphere of nitric oxide. There was no change in the optical spectrum of the parent complex. Nitric oxide characteristically adds to Fe(II) complexes, and the absence of a reaction in this case discounts the possibility of a tautomeric equilibrium involving Fe-PhenoxSQ electron transfer (eq 2) of



the type proposed for oxidatively active iron-catechol complexes.⁹ Further, a sample of Fe(PhenoxSQ)₂Cl was reduced with cobaltocene and exposed to an atmosphere of NO. The absence of a reaction in this case shows that reduction occurs at one of the PhenoxSQ ligands, rather than at the metal. A ligand oxidation reaction similar to that of Ru(PPh₃)Cl(PhenoxSQ)₂ was attempted by reducing Fe(PhenoxSQ)₂Cl with cobaltocene followed by exposure of the reduced solution to air. Several products were obtained from this reaction, but the only iron-containing product isolated in pure form was identified as Fe-(PhenoxSQ)₃. There are two significant differences between the chemistry with iron and the reaction described for the ruthenium

Table 6. Selected Bond Lengths and Angles for [Ni(PhenoxBQ)₂(NO₃)]⁺

Bond Lengths (Å)			
Nickel			
Ni-O1	1.998(7)	Ni-N2	2.075(6)
Ni-O3	1.968(4)	Ni-C5	2.173(9)
Ni-N1	2.116(7)	Ni-O6	2.115(5)
PhenoxSQ-1			
O1-C2	1.273(10)	C3-C4	1.373(11)
N1-C1	1.314(13)	C4-C5	1.427(12)
N1-C7	1.391(11)	C5-C6	1.381(14)
C1-C2	1.474(12)	C1-C6	1.424(11)
C2-C3	1.416(14)	C6-O2	1.382(10)
PhenoxSQ-2			
O3-C30	1.294(9)	C31-C32	1.381(11)
N2-C29	1.335(8)	C32-C33	1.433(12)
N2-C35	1.379(10)	C33-C34	1.378(9)
C29-C30	1.456(11)	C29-C34	1.425(10)
C30-C31	1.406(9)	C34-O4	1.398(10)
Bond Angles (deg)			
Nickel			
O1-Ni-O3	101.7(2)	O1-Ni-O5	155.6(2)
O3-Ni-O5	102.7(3)	O1-Ni-O6	95.2(2)
O3-Ni-O6	162.6(3)	O5-Ni-O6	60.4(3)
O1-Ni-N1	79.4(3)	O3-Ni-N1	90.2(2)
O5-Ni-N1	99.7(3)	O6-Ni-N1	88.7(2)
O1-Ni-N2	92.3(3)	O3-Ni-N2	81.0(2)
O5-Ni-N2	92.2(3)	O6-Ni-N2	102.7(2)
N1-Ni-N2	166.6(3)		
PhenoxSQ-1			
Ni-O1-C2	115.2(6)	N1-C1-C2	114.7(7)
O1-C2-C1	118.3(9)	Ni-N1-C1	111.3(5)
PhenoxSQ-2			
Ni-O3-C30	115.4(5)	N2-C29-C30	116.1(6)
O3-C30-C29	116.8(5)	Ni-N2-C29	110.5(5)

complex. The PPh₃ ligand of Ru(PhenoxSQ)₂(PPh₃)Cl provides steric direction for the steps associated with the oxidative cleavage of the PhenoxSQ ring and the subsequent formation of chiral centers in the product.^{4b} In the absence of this direction, the course of the reaction becomes considerably more complex. Second, chemical reduction of Ru(PhenoxSQ)₂(PPh₃)Cl occurs at the metal, while for Fe(PhenoxSQ)₂Cl the first reduction is ligand-based. The site of initial attack by dioxygen likely occurs at the reduced center of the molecule, and this may lead to differences in the course of ligand oxidation.

[Ni(PhenoxBQ)₂(NO₃)](NO₃). Interpretation of electrochemical couples as ligand- or metal-based processes can be facilitated by knowing how the ligands behave in the absence of an electroactive metal. Nickel complexes of the PhenoxBQ ligand have been investigated with this interest. Addition of PhenoxBQ to an ethanol solution of nickel(II) nitrate gave the green nitrate salt of the Ni(PhenoxBQ)₂(NO₃)⁺ cation. The complex has been characterized crystallographically; a view of the cation is shown in Figure 4. PhenoxBQ ligands are chelated with the metal ion with *trans* nitrogen atoms to give a structure that is similar to Fe(PhenoxSQ)₂Cl but with the chelated nitrate ligand occupying equatorial coordination sites. Carbon-oxygen bond lengths to the carbonyl oxygen of the iminobenzoquinone average 1.28(1) Å (Table 6). This value is slightly longer than the corresponding

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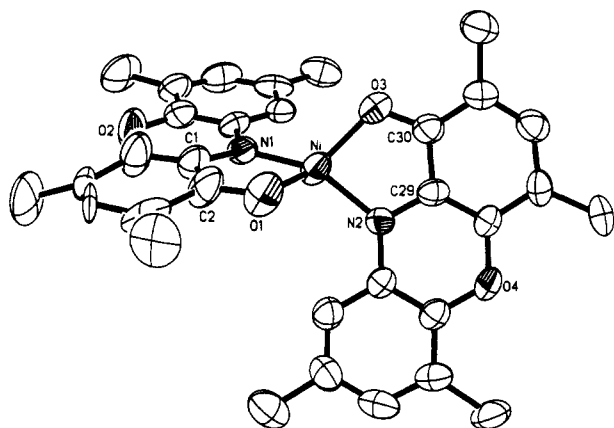


Figure 5. View of Ni(PhenoxSQ)₂.

bond of free PhenoxBQ, but coordinated benzoquinone ligands generally have C–O lengths that are longer than those of the free quinone. Similarly the iminoquinone C–N length 1.32(1) Å is 0.02 Å longer than that of PhenoxBQ. The pattern of C–C bond lengths about the quinone rings shows the expected localized single and double bonding typical of benzoquinones. However, the C–C double-bond lengths are slightly lengthened relative to the lengths of PhenoxBQ and structural differences between the free and coordinated PhenoxBQ ligands reflect subtle electronic changes that occur upon coordination. These further appear as shifts in infrared bands with the $\nu(\text{C–O})$ and $\nu(\text{C–N})$ vibrations appearing at 1617 and 1577 cm⁻¹ for the complex. As in the case of [Fe(PhenoxBQ)₂Cl]⁺ there is a dramatic change in color for the complex relative to the color and optical spectrum of free PhenoxBQ. Bands that appear at 393 (15 713 M⁻¹ cm⁻¹), 417 (8022), 516 (3000), and 810 nm (2667) for [Ni(PhenoxBQ)₂(NO₃)](NO₃) result in the green color. The magnetic moment of the complex is 3.27 μ_{B} , a value that is typical for octahedral Ni(II).

Ni(PhenoxSQ)₂. Reduction of the [Ni(PhenoxBQ)₂(NO₃)]⁺ cation with 2 equiv of cobaltocene produced a neutral complex product. Crystallographic analysis indicated that it was the four-coordinate molecule Ni(PhenoxSQ)₂ shown in Figure 5. Interactions between *tert*-butyl substituents of adjacent PhenoxSQ ligands preclude a coplanar arrangement of two ligands in a preferred square planar structure. Rather, Ni(PhenoxSQ)₂ has ligands oriented at right angles in a tetrahedral coordination geometry with a dihedral angle between ligand planes of 72°. A fold in the ligand plane results in slight disorder for carbon atoms of the semiquinone ring containing O1 and N1. One set of ring carbon atoms is shown in Figure 5, and the disorder gives irregularly shaped ellipsoids for these atoms. As with iron, reduction results in a decrease in $\nu(\text{C–O})$ and $\nu(\text{C–N})$ to 1530 and 1483 cm⁻¹. The electronic spectrum of Ni(PhenoxSQ)₂ consists of intense bands at 455 (15 350 M⁻¹ cm⁻¹), 529 (13 820), and 809 (5150). Reduction of the parent cation is accompanied by a dramatic change in the color of the solution from green to dark red. Strong antiferromagnetic coupling between the radical ligands and the paramagnetic Ni(II) ion results in diamagnetism for the molecule. Sharp *tert*-butyl resonances appear at 1.201, 1.306, 1.420, and 1.497 ppm in the ¹H-NMR spectrum, and resonances for ring protons appear at 7.6 and 7.7 ppm. Selected bond lengths and angles are listed for the complex in Table 7. Features of the PhenoxSQ ligands are similar to those of Fe(PhenoxSQ)₂Cl with an average C–O length of 1.29(1) Å and an average C–N length of 1.34(1) Å for bonds within the chelate rings. The Ni–N lengths average 1.909(6) Å, a value that is shorter than Ni–N lengths of tetrahedral Ni(α -diimine)₂ complexes, compounds that are generally viewed to contain Ni(0). Electrochemical characterization on Ni(PhenoxSQ)₂ shows a four-membered redox series that is qualitatively similar to the ligand-based couples of Fe(PhenoxSQ)₂Cl (Figure 3). Two oxidations

Table 7. Selected Bond Lengths and Angles for Ni(PhenoxSQ)₂

Bond Lengths (Å)			
Nickel			
Ni–O1	1.896(5)	Ni–N1	1.913(7)
Ni–O3	1.913(6)	Ni–N2	1.904(6)
PhenoxSQ-1			
O1–C2	1.297(13)	C3–C4	1.41(7) ^a
N1–C1	1.339(12)	C4–C5	1.27(4) ^a
N1–C7	1.395(10)	C5–C6	1.399(25)
C1–C2	1.412(14)	C1–C6	1.420(16)
C2–C3	1.34(4) ^a	C6–O2	1.370(13)
PhenoxSQ-2			
O3–C30	1.291(10)	C31–C32	1.380(12)
N2–C29	1.346(11)	C32–C33	1.411(12)
N2–C35	1.379(9)	C33–C34	1.393(12)
C29–C30	1.434(10)	C29–C34	1.406(11)
C30–C31	1.410(12)	C34–O4	1.401(9)
Bond Angles (deg)			
Nickel			
O1–Ni–O3	130.7(2)	O1–Ni–N1	83.5(3)
O3–Ni–N1	115.9(2)	O1–Ni–N2	111.7(2)
O3–Ni–N2	83.5(2)	N1–Ni–N2	139.0(3)
PhenoxSQ-1			
Ni–O1–C2	113.2(6)	N1–C1–C2	113.7(9)
O1–C2–C1	116.9(9)	Ni–N1–C1	112.7(5)
PhenoxSQ-2			
Ni–O3–C30	113.5(5)	N2–C29–C30	113.5(7)
O3–C30–C29	116.1(7)	Ni–N2–C29	113.0(5)

^a Sites of disorder.

appear at +0.232 and +1.524 V (vs NHE), and two reductions appear at –0.790 and –1.211 V.

Discussion

In its oxidized iminobenzoquinone form (IVa), PhenoxBQ appears to be a far better chelating agent than the *o*-benzoquinones. There are no stable benzoquinone or semiquinone complexes of iron or nickel that correspond to either the iminoquinone or iminosemiquinone complexes described in this study. The primary centers of electrochemical activity in complexes of both metals are the iminoquinone ligands. Reduction potentials of free PhenoxBQ and the ligands of Fe(PhenoxSQ)₂Cl and Ni(PhenoxSQ)₂ given in Table 5 show a strong positive shift upon coordination. Similar shifts occur for the benzoquinone ligands, and the potential ranges of the four-membered redox series of the RuL₂(DBQ)₂ complexes, where DBQ is the 3,5-di-*tert*-butyl-1,2-benzoquinone ligand in its various charged forms, are quite similar to those of the Fe and Ni complexes listed in Table 5.¹⁰ Reduction of the ligands at the metal is accompanied by low-energy shifts in C–O and C–N vibrational bands and changes in the magnetic properties of the complexes due to spin-spin coupling between the paramagnetic metal ion and the radical iminosemiquinone ligands. Reduction of Fe(PhenoxSQ)₂Cl was carried out to prepare a form of the complex that may undergo ligand oxidation upon exposure to dioxygen. The products of air oxidation formed as a complicated mixture of compounds, some containing iron, that are the result of nonselective rearrangement reactions. The PPh₃ of Ru(PPh₃)(PhenoxSQ)₂Cl is clearly important in directing the stereochemical changes in the reaction described in eq 1.

The similarity between the PhenoxBQ ligand and the reduced pterin cofactors that appear in specific metalloenzymes was described in the Introduction. Paramagnetic organic radical cofactors are being observed with increasing frequency in metalloenzymes.¹¹ EPR has served as a sensitive method of radical

detection. However, in cases where the association between cofactor and metal is intimate, strong spin-spin coupling may occur and the radical may be unobserved in a magnetic resonance experiment. The dihydropterin quinones undergo reduction at potentials that are slightly more positive than that of PhenoxBQ. For example, the BQ/SQ reduction potential of 2-amino-6,7,8-trimethyl-4-oxo-4,8-dihydropteridine quinone (V) has been reported at -0.52 V,⁸ compared with the PhenoxBQ/PhenoxSQ reduction at -0.85 V. Coordinated with Fe(III) the pteridine may be easily reduced to the semiquinone form, and such species may contribute to the mechanism for enzymatic dioxygen activation. Characterization on the PhenoxSQ complexes has shown that prominent low-energy charge-transfer transitions may

be observed, and similar low-energy bands may appear diagnostically for biological metal-pterinsemiquinone species. On the basis of these observations, optical spectroscopy may offer greatest promise for the identification of metal-coupled radicals in biological systems.

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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 Fe(PhenoxSQ)₂Cl, [Ni(PhenoxBQ)₂(NO₃)](NO₃), and Ni(PhenoxSQ)₂ (48 pages). Ordering information is given on any current masthead page.