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Iron(III), Manganese(III), and Cobalt(III) Complexes with Single Chelating *o*-Semiquinone Ligands

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The molecule $\mathrm{M^{II}}$(salen) reacts with *o*-quinones to give $\mathrm{M^{III}}$(salen)(*o*-SQ), where M is iron, manganese, or cobalt, salen is the dianion of *N,N'*-ethylenebis(salicylidenimine), and *o*-SQ is a semiquinone radical anion. In the case of iron, $\mathrm{Fe^{III}}$(salen)(*o*-SQ) complexes were formed with 1,2-naphthoquinone (1,2-NQ), 9,10-phenanthrenequinone (9,10-PhenQ), and 3,5-di-*tert*-butyl-*o*-benzoquinone (3,5-DBQ). All three of these complexes give ^{57}Fe Mössbauer spectra characteristic of high-spin iron(III) and have effective magnetic moments near 4.86 μ_B at 286 K. Thus, the complexes can be *formally* viewed as high-spin iron(III) complexes, in which the unpaired electron of the coordinated *o*-semiquinone is antiferromagnetically coupled to the five unpaired iron(III) electrons ($-J > 600$ cm^{-1}) to give complexes with $S = 2$ ground states. Intermolecular magnetic exchange interactions in the solid state are also present for the first two of these $\mathrm{Fe^{III}}$(salen)(*o*-SQ) complexes. Acenaphthenequinone (AceNQ) does not react with $\mathrm{Fe^{II}}$(salen), whereas, *o*-chloranil (*o*-chl) reacts to give $[\mathrm{Fe(salen)}]_2(\mathrm{Cl_4cat})$, a binuclear iron(III) complex bridged by the catechol dianion of *o*-chloranil. 1,2-Naphthoquinone, 3,5-di-*tert*-butyl-*o*-benzoquinone, and *o*-chloranil react with $\mathrm{Mn^{II}}$(salen). The compound $\mathrm{Mn^{III}}$(salen)(3,5-DBSQ) was isolated and found to have a μ_{eff} of 4.21 μ_B at 286 K, which is relatively temperature dependent down to 4.2 K and suggests the presence of three unpaired electrons resulting from an antiferromagnetic exchange interaction between the one unpaired electron of the 3,5-DBSQ ligand and the four unpaired electrons of the metal. $\mathrm{Co^{II}}$(salen) reacts only with 3,5-di-*tert*-butyl-*o*-benzoquinone and *o*-chloranil. The complex $\mathrm{Co^{III}}$(salen)(3,5-DBSQ) was isolated and characterized to have a single unpaired electron, with $\mu_{\mathrm{eff}} = 1.86$ and 1.74 μ_B at 286 and 4.2 K, respectively. The EPR spectrum of a room-temperature $\mathrm{CH_2Cl_2}$/toluene (50:50) solution of $\mathrm{Co^{III}}$(salen)(3,5-DBSQ) shows ^{59}Co and ^{1}H hyperfine splitting with coupling constants of 10.20 and 3.50 G, respectively. The ^{1}H hyperfine coupling constant of uncoordinated 3,5-DBSQ is 3.20 G, and since the ^{1}H coupling constant is assumed to be more diagnostic of the extent of electron transfer in complex formation, this complex is best described as a low-spin cobalt(III) complex with a coordinated semiquinone. $\mathrm{Co^{II}}$(salen) reacts with *o*-chloranil to give $[\mathrm{Co(salen)}]_2(\mathrm{Cl_4cat})$. The relative reactivities of the $\mathrm{M^{II}}$(salen) complexes with the various *o*-quinones are discussed.

Introduction

Quinones play an integral role in many biological electron-transfer processes, particularly respiration and photosynthesis.[4,5] During these processes, quinones are reversibly reduced to semiquinone radical anions, with the concomitant oxidation of divalent metal centers. Recent EPR data have shown that ubiquinone, a *p*-benzoquinone derivative known as coenzyme Q, interacts with the high potential iron–sulfur protein (Hipip) in mitochondria.[6] This particular quinone is thought to transfer an electron via the semiquinone form between various flavoprotein dehydrogenases and the collection of nonheme iron sulfur proteins and cytochromes in the electron transport chain. Additionally, an iron–ubiquinone couple has been identified as the primary electron acceptor in bacterial photosynthesis.[7] In this process, as in the electron-transport chain, ubiquinone functions as an electron shuttle, being initially reduced to the semiquinone form. Plastoquinone, another substituted *p*-benzoquinone, is known to be involved in the transfer of electrons from photosystem II to photosystem I during photosynthesis in green plants.[8] Catechols, totally reduced *o*-quinones, function as reductants in enzymatically catalyzed insertion and noninsertion reactions of oxygen.[9]

In view of the importance of quinones in electron-transport chains, it is desirable to characterize several iron complexes with quinone, semiquinone, or hydroquinone ligands. The redox function of the quinone has been well established.[10] However, relatively few investigations of quinones reacting with metal ions have been reported.[11] The synthesis and characterization of π complexes and electron donor–acceptor systems have been reported.[12] Several metal–quinone complexes in which the quinone moieties are σ bonded have also been reported.[13-15] Preparation of these σ complexes often involves oxidative addition of *o*-quinones to low-valent organometallic complexes.[16] Monomeric and dimeric complexes have been prepared from the reactions of metal carbonyls with *o*-quinones.[17] In most of these complexes, the quinones are not bonded as semiquinones. In fact, there are very few examples of metals chelated to semiquinone radical anions.[17,18] An EPR study of semiquinones complexed to $\mathrm{Zn^{2+}}$ and other diamagnetic metal ions was published in 1964.[19] EPR evidence for

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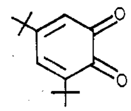
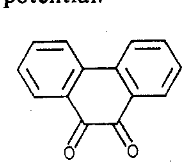
a cobalt–semiquinone system formed by the reaction of Co^{II}(salphen), where salphen is the *N,N'-p*-phenylenebis(salicylideniminato) ligand, and *o*-benzoquinone has been reported.[20] A similar cobalt system, (3,5-di-*tert*-butyl-*o*-benzosemiquinonato)(triethylenetetramine)cobalt(III) chloride, $[Co(trien)(DBSQ)]Cl_2$, has been isolated and characterized by infrared, visible, and EPR spectral data.[21] More recently, reports of metal ions tris ligated by semiquinones have appeared.[17] Unpaired electron density found in these molecules is most likely delocalized throughout the entire molecule.[22]

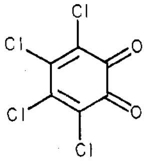
To further elucidate the electronic and molecular structure of transition-metal complexes with semiquinone ligands, we have synthesized and characterized a series of iron–, manganese–, and cobalt–semiquinone complexes. Following the method of Floriani et al.,[23,24] we have reacted Fe^{II}(salen), Mn^{II}(salen), and Co^{II}(salen), where salen is the dianion of *N,N'*-ethylenebis(salicylidenimine), with several *o*-quinones varying in oxidation potential.



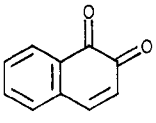
3,5-di-*tert*-butyl-*o*-benzoquinone (3,5-DBQ)



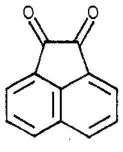
9,10-phenanthrenequinone (9,10-PhenQ)



o-chloranil (*o*-chl)



1,2-naphthoquinone (1,2-NQ)



acenaphthenequinone (AceNQ)

The resulting products have been characterized by several physical techniques, and the variation in reactivity of the *o*-quinone series across the M^{II}(salen) series has been determined.

Experimental Section

Physical Measurements. A Perkin-Elmer Model 457 spectrophotometer was used to obtain infrared spectra of samples prepared as Nujol mulls under argon. Visible spectral data were recorded on a Cary 14 UV–visible spectrophotometer.

Variable-temperature (4.2–286 K) magnetic susceptibility data were obtained with a Princeton Applied Research Model 150A vibrating sample magnetometer. A calibrated GaAs temperature-sensitive diode was employed to monitor the temperature in conjunction with a $CuSO_4 \cdot 5H_2O$ standard.

Iron-57 Mössbauer spectra for samples at 4.2 K were obtained on an instrument previously described.[25] Liquid-nitrogen and room-temperature spectra were run on a second instrument.[26] Computer fitting of ^{57}Fe Mössbauer data to Lorentzian lines was carried out with a modified version of a previously reported program.[27]

Electron paramagnetic resonance (EPR) spectra were recorded on a Varian E-9 X-band spectrometer equipped with an E101 microwave bridge. The magnetic field was calibrated with a 2,2-diphenyl-1-picrylhydrazyl sample purchased from Aldrich.

Mass spectra were recorded on a Varian MAT 731 field desorption mass spectrometer. All analytical data were obtained at the School of Chemical Sciences Microanalytical Laboratory, University of Illinois.

Compound Preparation. All reactions were performed under an atmosphere of purified argon. Argon was scrubbed of O_2 by MnO columns and then passed through 4A sieves to minimize the water content.[28] Schlenk apparatus was employed to prepare Fe^{II}(salen), Mn^{II}(salen), and Co^{II}(salen). Reactions leading to formation of the quinone adducts of these Schiff base complexes were accomplished in a Vacuum Atmospheres Corp. Dri-Lab equipped with an HE 493 Dri-Train.

Dimethylformamide (DMF) used in the synthesis of Fe^{II}(salen) and Co^{II}(salen) was shaken over KOH for 1 h, refluxed over BaO for 30 min, and fractionally distilled under N_2. The center cut (10–90%) was further distilled in vacuo. Cyclohexane, toluene, benzene, tetrahydrofuran (THF), and 2-methyltetrahydrofuran (2-MeTHF) were refluxed over sodium/benzophenone and distilled under argon. Bulk grade heptane was predried by chromatography over Alcoa F-20 alumina, before being distilled from Na/benzophenone under Ar. Acetone was warmed with $KMnO_4$, distilled, dried over Drierite for 48 h, decanted, and finally distilled under Ar. A 95% ethanol solution was distilled in air before use to remove trace metal impurities. All solvents were degassed in vacuo.

Technical grade 9,10-phenanthrenequinone purchased from Aldrich was purified via the bisulfite addition product.[29] Recrystallization from toluene yielded pure yellow-orange needles. Technical grade acenaphthenequinone was purified in a similar manner but recrystallized from acetic acid. 1,2-Naphthoquinone was prepared from β-naphthol as described in the literature.[30] 3,5-Di-*tert*-butyl-*o*-benzoquinone and *o*-chloranil were purchased from Aldrich and used without further purification.

Fe^{II}(salen). The parent salen ligand was synthesized by condensation of salicylaldehyde and ethylenediamine in 95% ethanol as described by Martell et al.[31] Fe^{II}(salen) was prepared by reacting the salen ligand with $Fe(CO)_5$, which had been freshly distilled and degassed under Ar. Ferrous salen prepared in this manner, as described by Calderazzo,[32] was found to be analytically purer than Fe^{II}(salen) synthesized from ferrous acetate.[33]

Mn^{II}(salen). A modification of a literature method was used to prepare Mn^{II}(salen).[33,34] In a typical preparation, salen (4.16 g, 15.5 mmol) was dissolved in 95% EtOH (200 mL) heated to 60 °C. A solution of $Mn(C_2H_3O_2)_2 \cdot 4H_2O$ (3.80 g, 15.5 mmol) in 95% EtOH (200 mL) heated to 60 °C was slowly added. The resulting orange solution was refluxed for 2 h, at which point a solution of NaOH (1.00 g, 25.0 mmol) in a minimum of 95% EtOH was added dropwise. The orange-red crystals which formed were allowed to stand overnight before being filtered. The crystals were first washed with 95% EtOH (50 mL) and then with acetone (50 mL) and finally dried in vacuo for 2 h.

Co^{II}(salen). This compound was synthesized in dimethylformamide via the method of Bailes.[35] Salen (10.0 g, 37.3 mmol) was dissolved in DMF (100 mL), heated to 60 °C, and added to a solution of $Co(C_2H_3O_2)_2 \cdot 4H_2O$ (9.28 g, 37.3 mmol) in DMF (150 mL) heated to 60 °C. The dark reddish brown crystals which immediately formed were allowed to stand overnight before being filtered, washed with acetone (50 mL), and vacuum dried for 2 h. Excellent analytical data were obtained for Co^{II}(salen), Fe^{II}(salen), and Mn^{II}(salen).

Fe(salen)(9,10-PhenSQ). This compound was prepared as described

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in Floriani et al.[23] Fe^{II}(salen) (1.10 g, 3.41 mmol) was added to a solution of 9,10-phenanthrenequinone (0.84 g, 4.03 mmol) in THF (80 mL). After the solution was stirred for 24 h, the black microcrystals were filtered, washed with THF (20 mL), and dried 1 h in vacuo. The yield was 1.36 g (75%).

Anal. Calcd for $C_{30}H_{22}N_2FeO_4$: C, 67.94; H, 4.18; N, 5.28; Fe, 10.53. Found: C, 67.65; H, 4.25; N, 5.17; Fe, 10.48.

Fe(salen)(1,2-NSQ). Fe^{II}(salen) (0.52 g, 1.61 mmol) was added to 1,2-naphthoquinone (0.27 g, 1.71 mmol) dissolved in THF (60 mL).[24] After being stirred for 24 h, the black mixture was filtered. A small quantity of black, powdery, THF-insoluble material remained on the frit. Cyclohexane (75 mL) was added to the filtrate, and after the solution stood for 1 h, the black microcrystalline semiquinone complex was filtered and dried for 1 h in vacuo. A yield of 0.40 g of compound was obtained (52%).

Anal. Calcd for $C_{26}H_{20}N_2FeO_4$: C, 65.02; H, 4.20; N, 5.83; Fe, 11.63. Found: C, 66.05; H, 4.29; N, 5.57; Fe, 11.11.

Fe(salen)(3,5-DBSQ). 3,5-Di-*tert*-butyl-*o*-benzoquinone (0.32 g, 1.45 mmol) was dissolved in THF (30 mL) and filtered. Fe^{II}(salen) (0.46 g, 1.43 mmol) was added, forming an intensely colored black solution. After the solution was stirred for 24 h, cyclohexane (50 mL) was added. Concentration of the solution to 40 mL by vacuum yielded black-brown microcrystals, which were filtered, washed with heptane (10 mL), and dried in vacuo for 1 h. The yield was 0.31 g (40%).

Anal. Calcd for $C_{30}H_{34}N_2FeO_4$: C, 66.43; H, 6.32; N, 5.16; Fe, 10.30. Found: C, 66.67; H, 6.44; N, 5.18; Fe, 10.17.

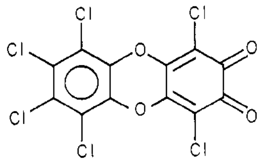
[Fe(salen)]$_2$(Cl$_4$cat). Fe^{II}(salen) (0.51 g, 1.59 mmol) was added to a filtered solution of *o*-chloranil (0.39 g, 1.59 mmol) in THF (30 mL). The dark reddish brown solution which formed was stirred for 10 min and filtered rapidly into heptane (75 mL) whereby a reddish brown material precipitated. The powdery material was filtered, washed with THF/heptane (50:50, 20 mL), and vacuum dried for 1 h. The yield was 1.19 g (84%).

Anal. Calcd for $C_{38}H_{28}N_4Cl_4Fe_2O_6$: C, 51.27; H, 3.17; N, 6.29; Cl, 15.93; Fe, 12.55. Found: C, 51.37; H, 3.56; N, 6.30; Cl, 15.49; Fe, 12.02.

[Fe(salen)Cl]$_2$. Fe^{II}(salen) (0.50 g, 1.55 mmol) was added to a solution of *o*-chloranil (0.45 g, 1.83 mmol) in THF (50 mL). The reddish brown solution was occasionally stirred for 48 h. The black crystals formed were filtered, washed with THF (10 mL), and dried in vacuo 1 h. A yield of 0.41 g of the ferric dimer was obtained (74%).

Anal. Calcd for $C_{32}H_{28}N_4Cl_2Fe_2O_4$: C, 53.74; H, 3.95; N, 7.83; Cl, 9.91; Fe, 15.62. Found: C, 53.80; H, 3.73; N, 7.83; Cl, 10.13; Fe, 15.77.

The THF filtrate was chromatographed on Brinkman silica gel (activity grade I, 0.05–0.2-mm particle size). 1,4,6,7,8,9-Hexachlorodibenzo-1,4-dioxin-2,3-quinone



eluted with the THF solvent front, while all [Fe(salen)Cl]$_2$ dissolved in the filtrate remained on the column. Evaporation of the effluent in the drybox yielded the orange-red chlorinated dioxinquinone, which analytical data indicated to contain a small quantity of THF. Field desorption mass spectrometry confirmed the molecular weight of the dioxinquinone. *Caution*! The above dioxin is extremely toxic, and it almost certainly is a powerful mutagen. IR (Nujol mull): $\nu_{C=O}$, 1680 (s) cm^{-1}; ν_{C-O-C}, 1028 (s) cm^{-1}. M^+ (mass spectrum): *m/e* 418, 420, 422, 424, 426.

Mn(salen)(3,5-DBQ). Mn^{II}(salen) (0.24 g, 0.75 mmol) was added to a filtered solution of 3,5-di-*tert*-butyl-*o*-benzoquinone (0.30 g, 1.36 mmol) in THF (30 mL). After the solution reacted for 48 h, it was filtered. Heptane (80 mL) was added, and the total volume was concentrated to 100 mL. The brown precipitate was filtered, washed with heptane (20 mL), and dried in vacuo 1 h. The yield was 0.21 g (52%).

Anal. Calcd for $C_{30}H_{34}N_2MnO_4$: C, 66.54; H, 6.33; N, 5.17; Mn, 10.14. Found: C, 66.24; H, 6.34; N, 5.16; Mn, 10.23.

Co(salen)(3,5-DBSQ). 3,5-Di-*tert*-butyl-*o*-benzoquinone (0.40 g, 1.82 mmol) was dissolved in THF (75 mL) and filtered. Co^{II}(salen) (0.50 g, 1.54 mmol) was added, and the mixture was stirred for 7 days. The mixture was filtered, and the green complex collected on the frit. Washing with cyclohexane (20 mL) followed by drying in vacuo for 1 h yielded 0.76 g of fluffy green semiquinone complex (91% yield).

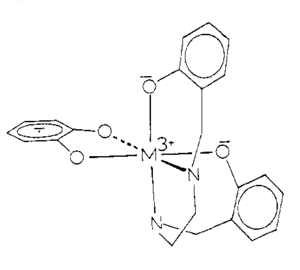
Anal. Calcd for $C_{30}H_{34}N_2CoO_4$: C, 66.05; H, 6.28; N, 5.13; Co, 10.80. Found: C, 65.71; H, 6.57; N, 5.06; Co, 10.40.

Reaction of *o*-Chloranil with Mn^{II}(salen) and Co^{II}(salen). Mn^{II}(salen) was found to react with *o*-chloranil in a manner similar to Fe^{II}(salen). After the initial formation of a dark solution, Mn(salen)Cl formed and was collected on a frit after a 7-day reaction time. Co^{II}(salen) reacted with *o*-chloranil over a period of 7 days to form the catechol complex [Co(salen)]$_2$(Cl$_4$cat). Satisfactory analytical data were obtained for this compound and the Mn(salen)Cl.

Results and Discussion

Compound Composition and Reactivities. Fe^{II}(salen), Mn^{II}(salen), and Co^{II}(salen) were chosen for this study because they are four-coordinate complexes which are very oxygen sensitive in solution.[32,34,35] Since these coordination complexes contain divalent metal ions which readily coordinate ligands in the fifth and sixth coordination sites, it was believed that formation of stable 1:1 metal–semiquinone adducts would be feasible. Additionally, it was thought that reacting a quinone with a readily oxidizable metal ion under anaerobic conditions should lead to the formation of "clean" products. The alternative method of reducing a catechol to a semiquinone appeared to be less favorable, for protonic solvents are required during the synthesis.

Two general types of products are obtained from the reaction of Mn^{II}(salen) with an *o*-quinone. If the redox potentials are appropriate, a one-electron oxidative addition of the *o*-quinone to the M^{II}(salen) complex occurs to give the 1:1 adduct M^{III}(salen)(*o*-SQ), which is suggested to possess a distorted octahedral coordination geometry. Stabilization of the semiquinone ligand appears to be facilitated by coordination through both oxygen atoms. It has been shown that the salen ligand can fold back in a M(salen) complex as a consequence of the chelation of the metal ion by a bidentate ligand.[37] The X-ray structure of *N,N'*-ethylenebis(salicylaldiminato)(acetylacetonato)cobalt(III) monohydrate supports this hypothesis.[38] This complex results from the reaction of Co^{III}(salen)I with Na^+acac^-.[39] In this reaction the cobalt ion remains in the trivalent state, the acetylacetonato ligand coordinates with both oxygen atoms, and the salen ligand adopts the rather unusual folded back conformation. It is quite likely, then, that the M^{III}(salen)(*o*-SQ) complexes studied in this work have the following molecular structure.



In addition to isolating these 1:1 adducts, we also observed the formation of 2:1 adducts, which are characterized as containing two trivalent metal–salen moieties bridged by the

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Table I. One-Electron Half-Wave Potentials, E_1, for the Reduction of Quinones to Semiquinones

quinone	E_1, V
tetrachloro-*o*-benzoquinone	+0.14[a,g]
3,5-di-*tert*-butyl-*o*-benzoquinone	−0.56[b,e]
1,2-naphthenequinone	−0.56[a,d] (−0.46)[c,f]
9,10-phenanthrenequinone	−0.66[a,d] (−0.55)[c,f]
acenaphthenequinone	(−0.81)[c,f]

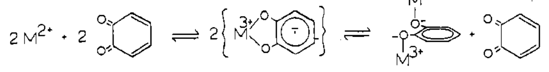
[a] Measured in acetonitrile solution with a supporting electrolyte of Et_4NClO_4. [b] Measured in acetonitrile solution with a supporting electrolyte of n-Bu_4NClO_4. [c] Measured in dimethyl sulfoxide solution with a supporting electrolyte of n-Bu_4NClO_4. [d] Reference 41. [e] Reference 42. [f] Reference 43. [g] Reference 13.

Table II. Iron-57 Mössbauer Parameters[a]

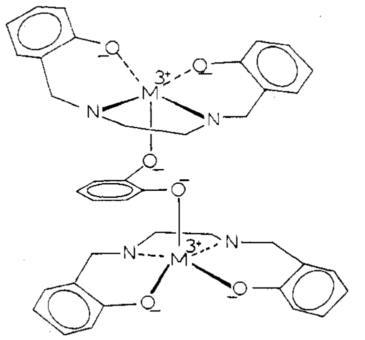
compd	T, K	δ,[b,c] mm/s	ΔE_Q,[c] mm/s	Γ,[b,d] mm/s
Fe(salen)(9,10-PhenSQ)	295	0.459 (2)	0.760 (2)	0.175 (2), 0.202 (2)
	295[e]	0.454 (4)	0.754 (4)	0.169 (4), 0.203 (6)
	100	0.548 (2)	0.781 (2)	0.179 (2), 0.211 (2)
	4.2	0.568 (2)	0.792 (2)	0.155 (1), 0.151 (1)
Fe(salen)-(1,2-NSQ)	4.2	0.539 (3)	0.829 (3)	0.274 (3), 0.270 (3)
Fe(salen)-(3,5-DBSQ)	295	0.40 (1)	0.87 (1)	0.22 (1), 0.29 (2)
	295[e]	0.43 (2)	0.81 (2)	0.24 (2), 0.29 (3)
	100	0.453 (8)	0.729 (8)	0.257 (4), 0.50 (1)
	4.2	0.543 (3)	0.902 (3)	0.217 (3), 0.262 (4)
$[Fe(salen)]_2$-(Cl_4cat)	295	0.38 (2)	1.04 (2)	0.35 (2), 0.36 (2)
$[Fe(salen)Cl]_2$[f]	295[e]	0.394 (6)	1.421 (6)	0.229 (4), 0.316 (8)
	100	0.506 (4)	1.421 (4)	0.217 (4), 0.271 (5)
	4.2	0.528 (1)	1.400 (1)	0.160 (1), 0.158 (1)
$[Fe(salen)Cl]_2$[g]	78[e]	0.51	1.40	

[a] Spectra run with 444-G external magnetic field unless denoted otherwise. [b] Relative to Fe metal. [c] Error in last significant figure in parentheses. [d] Half-width at half-maximum listed in order of increasing velocity of peak. [e] Spectrum run in absence of external magnetic field. [f] Synthesized from *o*-chloranil and Fe^{II}(salen) in this work. [g] Reference 48.

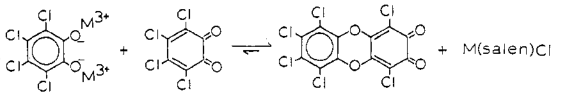
dianion of a catechol. The following reaction sequence is postulated to account for the formation of the 2:1 adducts,



which are suggested to have the following molecular structure.



The 2:1 metal–catechol complexes of iron and manganese that are derived from *o*-chloranil further react with free *o*-chloranil to yield a chlorinated dioxinquinone.



The relative reactivities of Fe^{II}(salen), Mn^{II}(salen), and Co^{II}(salen) with the various *o*-quinones have been determined in this work. The reduction potentials of the quinones range from −0.81 V for acenaphthenequinone to +0.14 V for *o*-chloranil, as is summarized in Table I. *o*-Chloranil due to the electron-withdrawing chloro groups has the highest oxidation potential, and, thus, it is more readily reduced than the other quinones investigated. In short, our experimental observations show that Fe^{II}(salen) is more reactive than Mn^{II}(salen), which exhibits a greater reactivity than Co^{II}(salen) to a given *o*-quinone.

Fe^{II}(salen) reacts with 9,10-PhenQ, 1,2-NQ, and 3,5-DBQ to yield 1:1 metal–semiquinone complexes over a period of 24 h. Attempts to isolate a semiquinone complex of *o*-chloranil proved futile, however. Reacting this high potential quinone with Fe^{II}(salen) in 1:1 stoichiometry leads to immediate formation of a 2:1 metal–catechol complex, $[Fe(salen)]_2(Cl_4cat)$. This catechol complex further reacts with free quinone, generated from the conproportionation reaction, to yield $[Fe(salen)Cl]_2$[44] and the dioxin–quinone. The reaction producing $[Fe(salen)Cl]_2$ is complete after approximately 3 h. In determination of this, Fe^{II}(salen) and *o*-chloranil were reacted in a 1:1 ratio over a period of 1 week. Portions of the mixture were filtered after 3 and 12 h and 1, 3, and 7 days. The filtrate from each filtration was immediately returned to the reaction mixture. Black-brown crystals of $[Fe(salen)Cl]_2$ which collected on the frit were dried in vacuo for 1 h and identified with analytical data. Reacting Fe^{II}(salen) with *o*-chloranil in exact 2:1 stoichiometry leads to formation of the 2:1 metal–catechol complex. Filtration of the reaction solution after 48 h yielded no $[Fe(salen)Cl]_2$. Addition of cyclohexane precipitated the reddish brown catechol complex, which exhibited an infrared spectrum and analytical data identical with that of the catechol complex isolated after 15 min from a 1:1 ratio of Fe^{II}(salen) and *o*-chloranil. Dissolving the catechol complex in the THF containing excess *o*-chloranil leads to rapid formation of $[Fe(salen)Cl]_2$. In the absence of free *o*-chloranil, then, the 2:1 iron–catechol complex appears to be relatively stable.

Mn^{II}(salen) was found to be less reactive toward the *o*-quinones. 9,10-Phenanthrenequinone does not appreciably react with Mn^{II}(salen) over a period of 10 weeks. A slight darkening of the quinone solution, in which Mn^{II}(salen) is suspended, occurs, indicating some metal–quinone complex formation. Filtration of the mixture yields only Mn^{II}(salen). 1,2-NQ and 3,5-DBQ react with the manganous Schiff base over a period of several days. Mn(salen)(3,5-DBSQ) was isolated from solution after a reaction time of 48 h. Mn^{II}(salen) reacts with *o*-chloranil in a manner similar to Fe^{II}(salen), rapidly forming the 2:1 manganese–catechol complex, $[Mn(salen)]_2(Cl_4cat)$, which further reacts with free *o*-chloranil to form Mn(salen)Cl.

Co^{II}(salen) is totally unreactive toward 9,10-phenanthrenequinone and fails to react with 1,2-naphthoquinone over a period of 4 weeks. It does form a 1:1 cobalt–semiquinone complex with 3,5-di-*tert*-butyl-*o*-benzoquinone after a 7-day reaction period. The reaction with *o*-chloranil is somewhat more rapid, as a 1:1 complex is formed after 2 days. Allowing the Co^{II}(salen) to react for 7 days results in formation of a 2:1 cobalt–catechol complex. This reaction time is much longer than that required for formation of the iron– and manganese–catechol complexes.

Mössbauer Spectroscopy. The high-spin ferric states of the iron ions are clearly established by ^{57}Fe Mössbauer data. All three iron–semiquinone complexes studied in this work are

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(44) Dimeric $[Fe(salen)Cl]_2$ is prepared in the reaction of salen and anhydrous $FeCl_3$. X-ray crystallography has shown that the complex is dimeric, and magnetic susceptibility measurements indicate an antiferromagnetic exchange interaction for the dimer with $J = -7.5$ cm^{-1}; see ref 35 and references therein. Monomeric Fe(salen)Cl has been isolated as a nitromethane solvate.

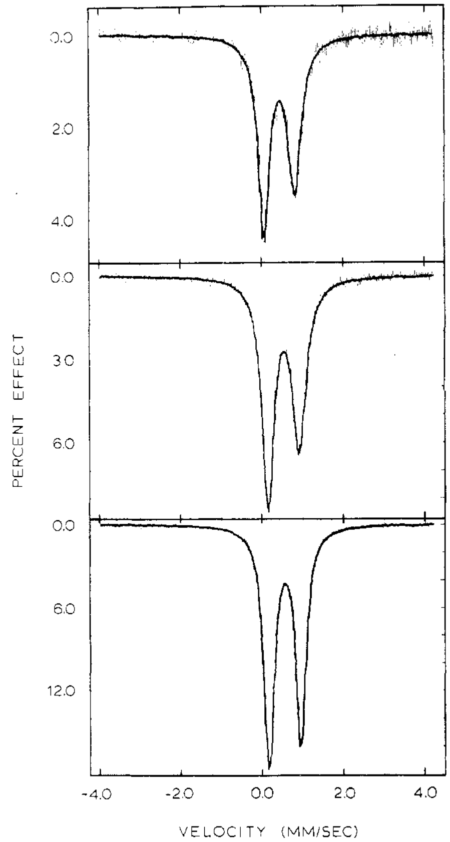

Figure 1. ^{57}Fe Mössbauer spectra for Fe(salen)(9,10-PhenSQ) recorded at 295 K (top), 100 K (middle), and 4.2 K (bottom).

characterized by single quadrupole-split doublets, with isomer shifts ranging from +0.40 to +0.57 mm/s (vs. iron, see Table II). These isomer shift values are well within the range expected for trivalent iron, and the quadrupole-splitting parameters substantiate the high-spin nature of each ferric ion.[45] In general, these Mössbauer parameters are very similar to those obtained for the binuclear ferric complexes previously prepared by reacting Fe^{II}(salen) with various *p*-quinones.[46,47] The catechol complex, [Fe(salen)]$_2$(Cl$_4$cat), exhibits a single doublet with a slightly greater quadrupole splitting of +1.04 mm/s at 295 K. This is in agreement with our premise that this complex most likely possesses square-pyramidal geometry, as opposed to the distorted octahedral coordination of the 1:1 iron–semiquinone adducts (vide supra). Mössbauer parameters obtained from the spectra of [Fe(salen)Cl]$_2$ are identical with the literature values,[48,49] within experimental error.

The Fe(salen)(1,2-NSQ) complex, isolated by filtration followed by precipitation with heptane, gives a clean quadrupole-split doublet. When we prepared the complex as described by Floriani,[24] however, we observed a spectrum with γ-ray absorption at three velocities. Undoubtedly, this spectrum represents a superposition of two quadrupole-split doublets, with the fourth peak being obscured. Fitting the data to three Lorentzian line shapes gave a quadrupole-split doublet, with $\Delta E_Q \approx 0.90$ mm/s, and an additional peak located approximately +0.29 mm/s from the low velocity component of the doublet. The quadrupole splitting for the doublet is quite similar to that obtained for pure Fe(salen)(1,2-NSQ). Hence, the additional, inner quadrupole-split doublet whose high velocity component is obscured is due to the THF-insoluble material collected on the frit during isolation of pure 1,2-NSQ adduct. As this material is insoluble in THF and other organic solvents such as toluene, it may well be polymeric in nature.

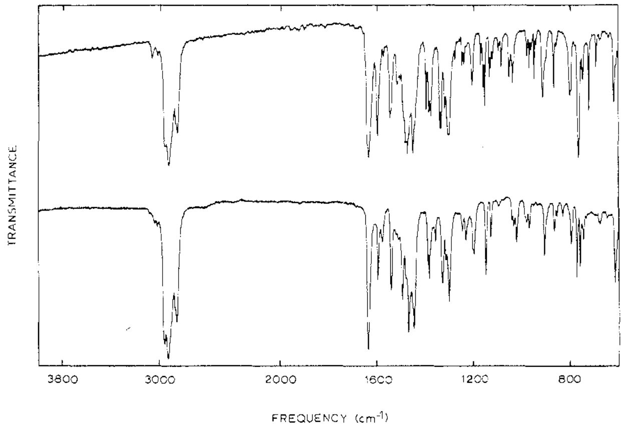

Figure 2. Nujol mull IR spectra of Fe(salen)(9,10-PhenSQ) (top) and Fe(salen)(3,5-DBSQ) (bottom).

At room temperature, Fe(salen)(3,5-DBSQ) exhibits an asymmetric quadrupole-split doublet, which maintains its asymmetry down to liquid-helium temperature. Fe(salen)-(9,10-PhenSQ), on the other hand, displays an asymmetric doublet which loses its asymmetry as the temperature is reduced (Figure 1). This temperature-dependent asymmetry is attributed to a magnetic broadening phenomenon.[50] This has been previously seen for ferric salen complexes with hydroquinone dianion bridges[46] and for other ferric complexes such as [Fe(salen)Cl]$_2$,[50] exhibiting temperature-dependent magnetic moments.

Infrared Spectroscopy. The reduction of the *o*-quinone in the 1:1 and 2:1 complexes is confirmed by the infrared spectra obtained as Nujol mulls. Free *o*-quinones are characterized by strong C=O stretching frequencies ranging from 1660 to 1700 cm^{-1}. 3,5-DBQ, dissolved in CCl$_4$, for example, shows two carbonyl bands, one at 1695 and one at 1670 cm^{-1}.[51] Upon reduction to the semiquinone, C=O stretching frequencies have been reported to shift approximately 150 cm^{-1} to a lower wavenumber. Matsunaga has demonstrated that the reduction of tetrabromo-*p*-benzoquinone (*p*-bromanil) to the semiquinone form with excess alkali iodide in acetone results in a C=O band shift of 180 cm^{-1}.[52] Further reduction to the dianion of the hydroquinone shifts this band from 1515 to 1420 cm^{-1}.[53] No bands above 1640 cm^{-1} are observed for any of the complexes isolated in this work, indicating the quinones have been reduced. Unfortunately, direct assignment of a C—O semiquinone stretching band is not possible.

Fe(salen)(3,5-DBSQ) exhibits a strong, sharp band at 1541 cm^{-1}, which is not observed for free 3,5-DBQ (Figure 2). However, IR bands for Fe(salen) are also observed in this region at 1525 and 1545 cm^{-1}.[30] In addition, because Fe(salen) displays a band at 1420 cm^{-1} and Nujol exhibits a 1450 cm^{-1} band, identification of a C—O band in this region cannot be made for the catechol complexes such as [Fe(salen)]$_2$(Cl$_4$cat) either. The infrared spectrum of [Fe(salen)Cl]$_2$ prepared from Fe^{II}(salen) and *o*-chloranil is identical with that of the dimeric chloride complex synthesized from salen and FeCl$_3$.[44] The Nujol mull IR spectrum of the chlorinated dioxin–quinone confirms the presence of ketone and ether functional groups.

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Table III. Effective Magnetic Moments per Metal Ion (μ_{eff}/M, μ_B)

compd	*T*, K 286	103	4.20
Fe(salen)(9,10-PhenSQ)	4.86	4.78	1.49
Fe(salen)(1,2-NSQ)	4.89	4.64	3.59
Fe(salen)(3,5-DBSQ)	4.87	4.85	4.39
[Fe(salen)]$_2$(Cl$_4$cat)	5.44	5.23	3.80
[Fe(salen)Cl]$_2$[a]	5.32	4.29	0.36
[Fe(salen)Cl]$_2$[b]	(5.32)[c]	(4.35)[d]	
Mn(salen)(3,5-DBSQ)	4.21	3.99	3.40
Co(salen)(3,5-DBSQ)	1.86	1.76	1.74

[a] Prepared from *o*-chloranil and Fe^{II}(salen) in this work. [b] Reference 48. [c] Actual measurement made at 296 K. [d] Actual measurement made at 122 K.

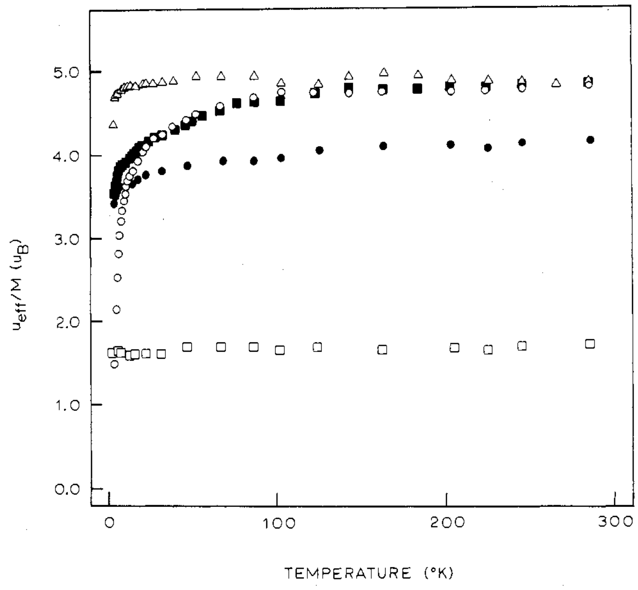

Figure 3. Effective magnetic moments per metal ion (μ_{eff}/M, μ_B) vs. temperature curves for Fe(salen)(3,5-DBSQ) (△), Fe(salen)(1,2-NQ) (■), Fe(salen)(9,10-PhenSQ) (○), Mn(salen)(3,5-DBSQ) (●), and Co(salen)(3,5-DBSQ) (□).

The molecule exhibits a strong C=O stretch at 1680 cm^{-1} and a C—O—C stretch at 1018 cm^{-1}, characteristic of aryl ethers. This latter band is completely absent from the spectrum of *o*-chloranil.

As can be seen in Figure 2, no OH stretching band is observed in the spectra of the M^{III}(salen)(*o*-semiquinone) complexes. This is in contrast to a recent report of the synthesis of Fe(salen)(catH), where catH is the monoanion of catechol.[54] This complex exhibits a band at 3380 cm^{-1}, which shifts to 2520 cm^{-1} when the catechol deuterated at the hydroxyl group is used as the reactant. The absence of an OH band in the spectra of our M^{III}(salen)(*o*-SQ) complexes substantiates the suggestion that these complexes have a distorted octahedral geometries. If only one of the semiquinone oxygen atoms were coordinated, protonation of the remaining oxygen to form an hydroxyl group would most likely occur.

Magnetic Susceptibility Data. The magnetic susceptibility data obtained for several semiquinone and catechol complexes are summarized in Table III. Fe(salen)(9,10-PhenSQ), Fe(salen)(1,2-NSQ) and Fe(salen)(3,5-DBSQ) all have effective magnetic moments (per iron) near 4.86 μ_B at 286 K. As is illustrated in Figure 3, Fe(salen)(3,5-DBSQ) exhibits little temperature dependence in the effective magnetic moment essentially down to liquid-helium temperature. Fe(salen)(9,10-PhenSQ) and Fe(salen)(1,2-NSQ) also exhibit temperature-independent magnetic moments down to liquid-nitrogen temperature, whereupon μ_{eff}/Fe decreases with decreasing temperature. The greatest reduction in μ_{eff}/Fe is exhibited by Fe(salen)(9,10-PhenSQ), where μ_{eff}/Fe decreases to 1.49 μ_B at 4.2 K. The attenuation in effective magnetic moments observed for these latter two iron complexes below the $S = 2$ spin-only value of 4.86 μ_B is attributable to antiferromagnetic *inter*molecular exchange interactions. Because 9,10-PhenSQ is a more extended semiquinone ligand than 1,2-NSQ, it is reasonable that *inter*molecular exchange interactions would be greater for Fe(salen)(9,10-PhenSQ) than for Fe(salen)(1,2-NSQ). In our recent work on a series of tris(semiquinone) complexes of iron(III), the 9,10-PhenSQ complex was found to exhibit the greatest *inter*molecular antiferromagnetic exchange interaction.[17] The X-ray structure[17] of Fe(9,10-PhenSQ)$_3$·9,10-PhenQ clearly shows the presence of intermolecular π-type stacking interactions. No *inter*molecular interactions were noted for Fe(3,5-DBSQ)$_3$, though, due to the presence of the bulky *tert*-butyl groups.

It is clear from the data illustrated in Figure 3 for the three Fe(salen)(*o*-SQ) complexes that the *intra*molecular antiferromagnetic exchange interaction is relatively strong. Thus, the single unpaired semiquinone electron is coupled to the five unpaired electrons associated with the ferric ion, producing an $S = 2$ ground state for the complex. There is no evidence for thermal population of the $S = 3$ excited state up to 286 K. If the interaction of the semiquinone unpaired electron with the ferric ion unpaired electrons is represented by the spin Hamiltonian $\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$, then least-squares fitting of the susceptibility data to the theoretical susceptibility equation for isotropic exchange interaction where $S_1 = {}^1/_2$ and $S_2 = {}^5/_2$ shows that the exchange interaction can be characterized by $-J > 600$ cm^{-1}. EPR spectroscopy studies[47,55] and M—O calculations[55] have conclusively shown that the unpaired *o*-semiquinone electron resides in a π-type molecular orbital. Depending on the particular *o*-semiquinone there are differing degrees of unpaired spin density on the oxygen atoms of the chelating *o*-semiquinone. It is conceivable that the magnetic exchange interaction of the *o*-semiquinone electron with the unpaired iron electrons is as weak as ca. 1000 cm^{-1}, if the unpaired spin density on the oxygen atoms is small.

The μ_{eff}/Mn vs. temperature data for Mn(salen)(3,5-DBSQ) are illustrated in Figure 3. There is little temperature dependence with μ_{eff}/Mn equal to 4.21 and 3.40 μ_B at 286 and 4.2 K, respectively. The antiferromagnetic interaction of the one *o*-semiquinone unpaired electron with the four manganese(III) unpaired electrons leads to an $S = {}^3/_2$ ground state and an $S = {}^5/_2$ excited state. The spin-only value of μ_{eff} for three unpaired electrons is 3.92 μ_B. It is likely that the 4.21 μ_B experimental value reflects some small amount of orbital angular momentum in the $S = {}^3/_2$ ground state of Mn(salen)(3,5-DBSQ).

Magnetic susceptibility measurements for Co(salen)(3,5-DBSQ) show that it is a simple paramagnet with an $S = {}^1/_2$ ground state (see Figure 3). The complex is characterized by μ_{eff} values of 1.86 μ_B at 286 K and 1.74 μ_B at 4.2 K. No appreciable intermolecular exchange interactions are observed for this complex or for the analogous manganese complex.

[Fe(salen)]$_2$(Cl$_4$cat) is characterized by a weak antiferromagnetic exchange, very similar to that seen for ferric salen moieties bridged by the dianion of a hydroquinone (see Table III for the data).[46] Some difficulty was encountered in fitting the experimental data to the theoretical equation for exchange

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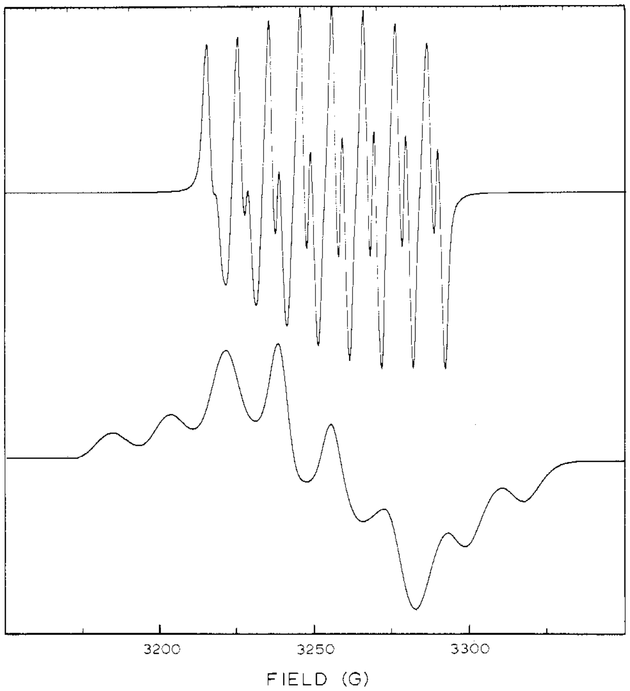

Figure 4. X-Band EPR spectra of Co(salen)(3,5-DBSQ) as a room-temperature CH_2Cl_2/toluene (1:1) solution (top) and as a liquid-nitrogen CH_2Cl_2/toluene (1:1) glass (bottom).

interaction in a binuclear high-spin ferric complex. A J value of $-0.65\ cm^{-1}$ was calculated by employing a g value of 1.90 and no zero field splitting. This small J value discounts the possibility that the two ferric ions are bridged by a single oxygen atom of the catechol dianion. μ-Oxo-bridged ferric Schiff base complexes generally have much larger J values (approximately $95\ cm^{-1}$).[35] It is also important to note that *o*-quinones have been found to coordinate only via the oxygen atoms in σ fashion[11,17,57] as opposed to *p*-quinones which may coordinate in a π manner.[11,12] Hence, we suggest a structure for $[Fe(salen)]_2(Cl_4cat)$ in which the ferric ions have square-pyramidal geometries and are coordinated to two different oxygen atoms of the bridging catechol dianion.

Electron Paramagnetic Resonance Spectroscopy. Fe(salen)(9,10-PhenSQ), Fe(salen)(1,2-NSQ), and Fe(salen)(3,5-DBSQ) are EPR silent, as expected for $S = 2$ systems. No signals were observed for powders, 2-MeTHF solutions, or frozen glass samples. Mn(salen)(3,5-DBSQ) displays a very broad isotropic signal centered at $g = 2.58$, as a powder at room and liquid-nitrogen temperatures. The signal is spread out over 7000 G at room temperature.

X-Band EPR spectra of Co(salen)(3,5-DBSQ) confirm the formulation of the complex as a semiquinone complex of cobalt(III) (see Figure 4). The spectrum of a room-temperature CH_2Cl_2/toluene (50:50) solution shows an isotropic signal consisting of a pattern of eight doublets. The interaction of the cobalt-59 $I = {}^7/_2$ nucleus with the unpaired electron spin results in the eight-line pattern. Further splitting of this pattern into the doublet pattern results from coupling of the proton para to the oxygen. The signal, centered at exactly $g = 2.00$, has ^{59}Co and ^1H hyperfine coupling constants of 10.20 and 3.50 G, respectively. The same sample, when run as a frozen glass at liquid-nitrogen temperature, displays a broader eight line apparently isotropic signal, with a ^{59}Co coupling constant of 17.50 G and no resolved ^1H hyperfine. The powder spectrum of Co(salen)(3,5-DBSQ) consists of a single sharp derivative, centered at $g = 2.00$ with no detectable hyperfine structure. $[Co(salen)]_2(Cl_4cat)$ as a room-temperature powder displays a signal very similar to that seen for the Co(salen)(3,5-DBSQ) glass. An eight-line hyperfine pattern with a ^{59}Co coupling constant of 17.50 G and no ^1H hyperfine is observed. This signal is most likely due to a small amount of 1:1 cobalt–semiquinone complex, in which conproportionation to the 2:1 cobalt–catechol complex and free quinone has not occurred. Since formation of the catechol complex is relatively slow, it is reasonable to assume that a small amount of cobalt–semiquinone adduct is present in the isolated catechol complex. Essentially, the cobalt–semiquinone impurity is doped into the diamagnetic catechol host.

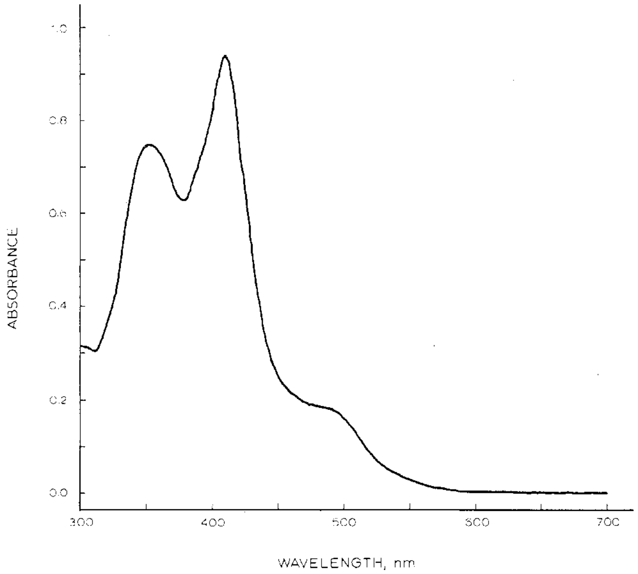

Figure 5. Electronic absorption spectrum of Co(salen)(3,5-DBSQ) dissolved in benzene.

The extent of electron transfer during formation of 1:1 metal–semiquinone complexes is reflected by the magnitude of the proton hyperfine coupling constant. The proton coupling constant, 3.50 G, for Co(salen)(3,5-DBSQ) is very similar to the proton coupling constant, 3.20 G, of free 2,5-di-*tert*-butyl-*o*-benzosemiquinone formed by electrochemical reduction of the quinone.[42] A linear relationship between unpaired π-electron density and the proton hyperfine splitting in π-type organic radicals has been established by McConnell.[58] This relationship is $a = QP$, where a is the proton coupling constant, Q is a proportionality constant, and P is the unpaired π-electron density in a p orbital orthogonal to the p orbital polarizing the proton spin density. The proton coupling constant is effectively a measure of the spin density induced at the proton nuclei by the unpaired π-electron density. Therefore, any alteration in π-electron density is reflected by a change in the coupling constant via a spin polarization mechanism. It is anticipated that the proton coupling constant is a much more direct measure of unpaired π-electron density than the cobalt coupling constant. A comparison of the proton coupling constant observed for the cobalt complex with the coupling constant seen for the free semiquinone indicates that the unpaired electron in Co(salen)(3,5-DBSQ) is largely localized on the *o*-semiquinone ligand.

Electronic Absorption Spectroscopy. The 1:1 metal–semiquinone and 2:1 metal–catechol complexes have rather interesting spectra in the 700–300-nm region. Co(salen)(3,5-

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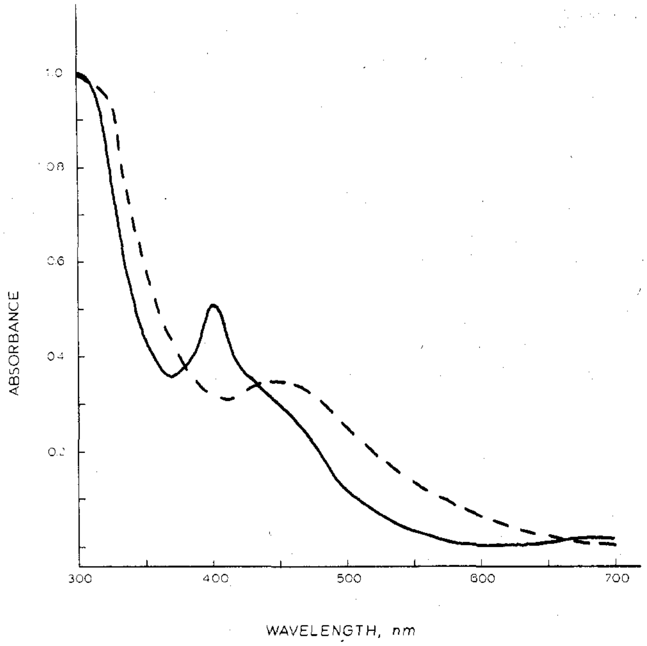

Figure 6. Electronic absorption spectra of benzene solutions of Fe(salen)(9,10-PhenSQ) (—) and $[Fe(salen)]_2(Cl_4cat)$ (---).

DBSQ) in benzene is characterized by three absorption bands with maxima at 494, 416, and 352 nm (see Figure 5). A change in the solvent to more polar THF and CH_2Cl_2 leads to a shift in the 416-nm band to 409 nm, while the other two bands remain unchanged. $[Co(salen)]_2(Cl_4cat)$, however, shows only a broad absorption band centered at 402 nm and a considerably less intense band at 452 nm.

The complex Mn(salen)(3,5-DBSQ) dissolved in benzene gives a spectrum consisting of two broad absorption bands at 487 and 347 nm and a more intense band located near 295 nm. The 295-nm band is shifted to 300 nm when the spectrum is taken in CH_2Cl_2.

The spectrum of Fe(salen)(9,10-PhenSQ) in benzene consists of a broad absorption at 463 nm, a sharp band at 402 nm, and a more intense band near 299 nm (Figure 6). In addition, a barely discernible band centered near 430 nm is present. When the solvent is changed to THF, the 402-nm band is shifted to 394 nm, while the 299-nm band is shifted to 325 nm. Fe(salen)(1,2-NSQ) in benzene is characterized by three bands at 463, 430, and 298 nm, while Fe(salen)(3,5-DBSQ) in benzene has several absorption bands, with maxima at 613 (w), 489, 452 (sh), 425, 357 (sh), and 302 nm. The intense band at 302 nm is shifted to 308 nm when the spectrum is taken in THF. The iron–catechol complex, $[Fe(salen)]_2(Cl_4cat)$, shows only a broad band centered around 450 nm and a more intense band at 303 nm (Figure 6). None of these absorptions are due to transitions within the iron orbital framework, as all d → d transitions are spin forbidden for high-spin ferric ions. These absorptions, then, are best assigned as metal → ligand and ligand → metal charge-transfer bands. It is significant to point out that dioxygenases and pyrocatechases, enzymes which catalyze the cleavage of catechols to *cis,cis*-muconic acid, are characterized by a broad absorption band with maximum around 450 nm. The active site in each of these enzymes contains a high-spin ferric iron.[9,59]

Summary and Comments

Fe^{II}(salen), Mn^{II}(salen), and Co^{II}(salen) initially react with various *o*-quinones via a one-electron redox reaction to form 1:1 metal–semiquinone complexes. Fe^{II}(salen) reacts more readily than Mn^{II}(salen), which is more reactive than Co^{II}(salen). This trend in oxidation tendency (Fe(III) > Mn(II) > Co(II)) has been demonstrated for divalent metal tetraphenylporphyrin systems.[60,61]

The 1:1 metal–semiquinone complexes undergo a disproportionation reaction to form 2:1 metal–catechol complexes and free quinone. While we have demonstrated this reaction for complexes formed from *o*-chloranil, we propose that it is general for all quinones and is controlled by the reduction potential of the semiquinone. Recently, a similar conproportionation reaction between the quinone–quinol units and semiquinone radical anions of melanin has been postulated.[62] Metal ions, particularly Zn^{2+}, were found to disturb the equilibrium between semiquinones and their oxidized and reduced forms. The ability of metal ions to stabilize the semiquinone radical anions has been established.[18,19] The rapid formation of the 2:1 metal–catechol complex of *o*-chloranil is due to the large reduction potential of the chlorinated semiquinone species.

Manganese- and iron–catechol complexes of *o*-chloranil further react with free *o*-chloranil to form Mn(salen)Cl or $[Fe(salen)Cl]_2$ and 1,4,6,7,8,9-hexachlorodibenzo-1,4-dioxin-2,3-quinone. A metal assisted nucleophilic attack of the tetrachlorinated catechol on the *o*-chloranil is postulated to occur. *o*-Chloranil is known to interact with its catechol in a coupled dehydrogenation, dehalogenation reaction to form the chlorinated dioxinquinone and hydrogen chloride.[63] This reaction, which proceeds slowly, is evidently enhanced by the presence of Fe(III) and Mn(III) ions. The same reaction sequence occurs when Fe^{II}(salen) is reacted with *o*-bromanil. In the absence of excess free quinone, the iron(III)– and manganese(III)–catechol complexes appear to be relatively stable in solution. The dimerization of *o*-benzoquinone to dibenzo-1,4-dioxin-2,3-quinone anion in alkaline alcoholic solution has been reported.[64]

No reaction was observed between acenaphthenequinone and any of the divalent metal Schiff base complexes. We initially thought that perhaps acenaphthenequinone does meet the stereochemical requirement for coordination, as it is the only nonbenzenoid quinone. This argument has been made for the failure of acenaphthenequinone to complex various metal halides.[65] The C_1–C_2 bond distance in acenaphthenequinone has been reported to be 1.53 Å.[66] However, the corresponding C–C bond distance in 9,10-phenanthrequinone has recently been determined to be 1.54 Å.[17] Thus, as the bidentate "bite" of these two quinones is very similar, this line of reasoning does not appear to be particularly valid. A better explanation for the failure of acenaphthenequinone to undergo a redox reaction is that the reduction potential of the quinone is too low. This quinone is a substantially weaker oxidant than the other *o*-quinones. We wish to note that reduction to the acenaphthenesemiquinone, however, has been accomplished with metallic zinc, as determined by EPR spectroscopy.[55]

As a final comment, it is interesting to point out the similarity in electronic properties between the 1:1 metal–semiquinone complexes and 1:1 metal–dioxygen adducts. Considerable interest and controversy have been generated by iron–, manganese–, and cobalt–dioxygen complexes.[67] On the basis of analysis of EPR data, 1:1 cobalt–dioxygen adducts

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have been formulated as $Co^{III}O_2^-$ species.[68] Similarly, an $Fe^{III}O_2^-$ formulation has been invoked to describe the bonding of O_2 to divalent iron.[69] The bonding of O_2 is proposed to involve transfer of an electron from the O_2 moiety, formally oxidizing the iron to the trivalent state and reducing the O_2 to coordinated superoxide. The interaction has been characterized as (1) donation to a lone pair of electrons from the sp^2 rehybridized superoxide orbital into the empty d_{z^2} iron orbital and (2) coupling of the superoxide unpaired electron with the unpaired iron electron by overlap of a π^* orbital of O_2^- with the half-filled d_{xz} iron orbital.[60] This electron coupling has been viewed as an antiferromagnetic exchange coupling, as in the Weiss proposal,[69] and also as a "significant bonding" interaction.[60] Recently it has been proposed[70] that a spin polarization mechanism is operative resulting in the relatively large cobalt hyperfine interaction. In this view of the interaction there is no necessity to transfer an electron from the Co(II) to the O_2.

In this work, we have observed complete electron transfer from Fe(II), Mn(II), and Co(II) to *o*-quinones upon coordination, yielding $M^{III}SQ^-$ complexes. The EPR results for Co(salen)(3,5-DBSQ) indicate the complete oxidation of Co(II) to Co(III) with the concomitant reduction of the dibutylated quinone to the semiquinone. This electron transfer is found to be essential for the *o*-quinone coordination. In the case of the iron and manganese systems, complete coupling of the semiquinone electron to the metal center occurs via a strong antiferromagnetic exchange interaction.

No molecular structural similarity between the semiquinone complexes and the O_2 adducts of analogous iron and cobalt complexes may be drawn, however. Dioxygen is known to bond in Fe and Co complexes in an end-on manner. Semiquinone coordination occurs through both oxygen atoms, analogous to the Griffith model of O_2 binding. This type of oxygen bonding has been indicated for porphyrin complexes of manganese, in which the O_2 appears to be coordinated as a peroxide, i.e., $Mn^{IV}O_2^{2-}$.[71]

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Registry No. Fe(salen)(9,10-phenSQ), 72796-12-4; Fe(salen)(1,2-NSQ), 72796-13-5; Fe(salen)(3,5-DBSQ), 72796-14-6; $[Fe(salen)]_2(Cl_4cat)$, 72796-15-7; $[Fe(salen)Cl]_2$, 15308-73-3; 1,4,6,7,8,9-hexachlorodibenzo-1,4-dioxin-2,3-quinone, 65005-72-3; Mn(salen)(3,5-DBSQ), 72796-16-8; Co(salen)(3,5-DBSQ), 72796-17-9; $[Co(salen)]_2(Cl_4cat)$, 72796-18-0; Mn(salen)Cl, 53177-12-1; Fe^{II}(salen), 14167-12-5; Mn^{II}(salen), 36026-26-3; Co^{II}(salen), 36870-54-9.

Supplementary Material Available: Tables IV-VIII of experimental magnetic susceptibility data (5 pages). Ordering information is given on any current masthead page.

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Stereochemically Nonrigid Silanes, Germanes, and Stannanes. 8.[1] Tetracyclopentadienyl and Tetrakis(methylcyclopentadienyl) Derivatives of Germanium(IV) and Tin(IV)

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The compounds GeR_4 (R = C_5H_5 or $C_5H_4CH_3$) have been synthesized, making possible a comparison with the already known tin analogues by IR, NMR, and mass spectroscopy. Attempts to prepare corresponding silicon or lead derivatives were unsuccessful; however, the species $M(C_5H_5)_3Cl$ (M = Ge or Sn) have also been characterized, and the influence of chloro substitution at the tin center on $^{117,119}Sn-H$ coupling constants and on ^{119m}Sn Mössbauer parameters is commented on. The temperature dependence of ^{13}C as well as ^1H NMR spectra for the MR_4 derivatives has been investigated, and the intramolecular rearrangement behavior in the methylcyclopentadienyl compounds has been rationalized. The spectral changes observed for $Ge(C_5H_4CH_3)_4$ are consistent with degenerate exchange between identical configurations resulting from equilibrium preponderance of a preferred nongeminal arrangement.

Introduction

Homoleptic compounds formed between quadrivalent tin and cyclopentadiene or methylcyclopentadiene were isolated in 1965 by Fritz and Kreiter.[2] These authors deduced from variable-temperature NMR spectroscopy that while in $Sn(C_5H_5)_4$ (**1**) a rapid rearrangement process led to equivalence among all ^1H nuclei in the molecule, the methylcyclopentadienyl analogue (**2**) showed no corresponding dynamic behavior. This conclusion[2,3] was subsequently argued to be incorrect by Davison and Rakita,[4] and as a result of a further study by Campbell and Green,[5] it is now clear that $Sn(C_5H_4CH_3)_4$ (**2**) exhibits the kind of behavior we[6,7] have termed *quasi-fluxional*, i.e., undergoes nondegenerate intramolecular rearrangement. The original controversy[2,4] can be attributed to the rapidity of metallotropic shifts in both compounds **1** and **2** as a result of which no conspicuous spectral changes occur within an accessible temperature range. The molecular and crystal structure of compound **1** has been determined by

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