Inorg. Chem. **1983**, *22*, 2545–2552

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Iron(III) Complexes with Semiquinone and Hydroquinone Ligands

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Received December 21, 1982

The results of the reactions of two different *p*-quinones and two different *o*-quinones with Fe^{II}(salpren), Fe^{II}(saloph), Fe^{II}(salprenOH), and Fe^{II}(saldien) are given. The ligands salpren, saloph, salprenOH, and saldien are the dianionic forms of the ligands that result from the condensation of 1 mol of salicylaldehyde with 2 mol of 1,3-diaminopropane, *o*-phenylenediamine, 1,3-diamino-2-hydroxypropane, and diethylenetriamine, respectively. The complexes Fe^{II}(salpren) and Fe^{II}(saloph) react with *o*-quinones to give high-spin ferric complexes with a chelated *o*-semiquinone ligand. Binuclear ferric complexes bridged by the dianion of the hydroquinone result from the reaction of either Fe^{II}(salpren) or Fe^{II}(saloph) with *p*-benzoquinone. The reaction of Fe^{II}(saloph) with 2,6-di-*tert*-butyl-1,4-benzoquinone gives the first example of a high-spin ferric complex with a monodentate *p*-semiquinone ligand. The complex Fe^{II}(salprenOH) reacts with either *o*-quinones or *p*-quinones to give the dimeric ferric complex [Fe^{III}(salprenO)]$_2$·THF; the quinone reactant is converted to hydroquinone. The only product that could be isolated in the case of Fe^{II}(saldien) reacting with quinones was a binuclear ferric complex bridged by a hydroquinone dianion. Magnetic susceptibility, IR, and Mössbauer data are presented.

Introduction

Quinones can potentially bond to metal ions in three different oxidation states: quinone, semiquinone, or hydroquinone. Interactions between iron ions and "quinone" species have been noted for several important biological systems such as the electron-transport chains involved in photosynthesis and respiration and at the active sites of oxygenases. Plastoquinone, a substituted *p*-benzoquinone, is known to be involved in the transfer of electrons from photosystem II to photosystem I during photosynthesis in green plants.[3] Ubiquinone, another substituted *p*-benzoquinone, interacts with the high-potential iron–sulfur protein (HiPIP) in mitochondria.[4] This quinone is thought to transfer an electron via the semiquinone form between various flavoprotein dehydrogenases and the collection of non-heme iron–sulfur proteins and cytochromes in the respiratory electron-transport chain. An iron–ubiquinone couple has also been identified as the primary electron-acceptor site in bacterial photosynthesis.[5] In this site two ubiquinone moieties are in close proximity to one high-spin iron(II) ion. The two ubiquinones shuttle between quinone and semiquinone forms, whereas the iron remains in the high-spin ferrous form.

In the case of dioxygenases, catechol binds to an iron ion and the two atoms from molecular oxygen are incorporated into the catechol.[6] In an earlier mechanism[7] for this process, the catechol interacts with a ferric ion, reducing the ferric ion to produce a ferrous ion–semiquinone association. Dioxygen is then activated by oxidatively adding to the ferrous ion to give a ferric site with coordinated semiquinone and superoxide ligands. An alternative mechanism has been postulated wherein catechol binds to a ferric ion through only one hydroxyl group.[8] The monodentate catecholate ligand is further activated by deprotonation of the second hydroxyl group. It is proposed that in this activated form the catecholate dianion reacts directly with dioxygen and the iron ion stays in the ferric state throughout the cycle.

The present study is a continuation of an ongoing program to characterize a number of iron complexes with quinone, semiquinone, or catecholate ligands. Tris(*o*-semiquinone) complexes of high-spin iron(III) have been reported,[9] as have high-spin iron(III) complexes with a single *o*-semiquinone ligand.[10] Recently we prepared a number of high-spin iron(III) complexes, each of which have one chelated *o*-semiquinone ligand and one chelated catecholate ligand.[11] The reaction of *p*-quinones with either Fe^{II}(salen),[12] where salen is the dianion of *N,N'*-ethylenebis(salicylideneamine), or Fe^{II}(TPP),[13] where TPP is the dianion of *meso*-tetraphenylporphyrin, gives binuclear iron(III) complexes with bridging hydroquinone dianions. Heistand et al.[14] recently reported the X-ray structure of one of the salen compounds (μ-1,4-benzenediolato-*O,O'*)bis[*N,N'*-ethylenebis(salicylideneaminato)iron(III)], which they formed by the reaction of Fe^{III}(salen)(OAc) with hydroquinone. They also reported the preparation and crystal structure of an iron(III) complex with a monodentate catecholate ligand, Fe(saloph)(catH), where saloph is the dianion of *N,N'*-(1,2-phenylene)bis(salicylideneamine) and catH is the monoanion of catechol.

Results and Discussion

Compound Compositions and Reactivities. In our previous studies the reactions of *o*-quinones and *p*-quinones with Fe^{II}(salen) and Fe^{II}(TPP) were investigated. Four different iron(II) complexes were selected for the present study:

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(1) Université Paul Sabatier.

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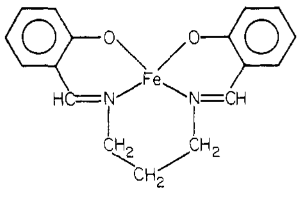
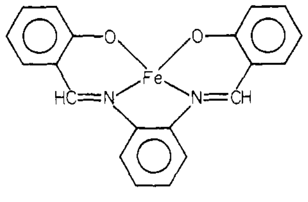


Fe^{II}(salpren)



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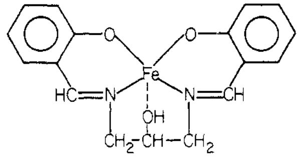

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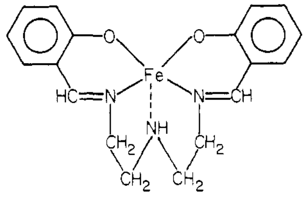
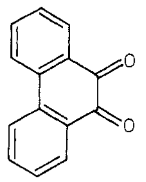
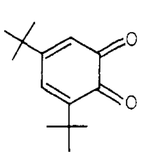
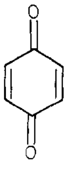
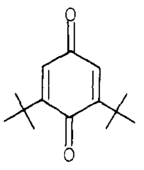


Fe^{II}(saldien)

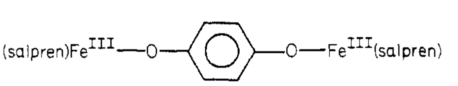
These iron(II) complexes were reacted with several *o*-quinones and *p*-quinones, including

9,10-PhenQ 3,5-DtBQ *p*-BQ 2,6-DtBQ

The above series of iron(II) complexes represent interesting changes in the flexibility and the chemical nature of the bridge between the two imine nitrogen atoms compared to the case of Fe^{II}(salen). Oxidative addition of an *o*-quinone to Fe^{II}(salen) leads to a folding of the salen ligand to accomodate the chelating *o*-semiquinone ligand in the Fe^{III}(salen)(*o*-semiquinone) product.[15] In this regard it was of interest to see the influence of the added inflexibility associated with the *o*-phenylene moiety in Fe^{II}(saloph). The complexes Fe^{II}(salprenOH) and Fe^{II}(saldien) each have an additional basic site which might serve as a ligand atom and therefore affect the ability of an *o*-quinone to oxidatively add to the iron(II) complex.

The complex Fe^{II}(salpren) reacts over a 36-h period in THF with 9,10-PhenQ and 3,5-DtBQ to give *o*-semiquinone complexes with the composition Fe^{III}(salpren)(*o*-semiquinone). The reaction of Fe^{II}(salpren) with *p*-BQ gives a binuclear ferric complex bridged by the dianion of the hydroquinone:



We were not able to characterize a metal-quinone complex from the reaction of Fe^{II}(salpren) and 2,6-DtBQ. As anticipated, Fe^{II}(salpren) reacts in the same manner as Fe^{II}(salen).

It was interesting to find that Fe^{II}(saloph) reacts with 9,10-PhenQ and 3,5-DtBQ in the same manner as Fe^{II}(salpren) to give 1:1 iron(III)-(*o*-semiquinone) complexes. The expected binuclear ferric complex bridged by hydroquinone dianion froms with *p*-BQ. The most unusual complex results, however, from the reaction of Fe^{II}(saloph) with 2,6-DtBQ. This reaction gives the first high-spin ferric complex with a monodentate *p*-semiquinone. Apparently the two *tert*-butyl substituents in the 2- and 6-positions of the quinone reactant block the formation of the usual binuclear ferric complex. The dark green semiquinone complex Fe^{III}(saloph)(2,6-DtBSQ) decomposes readily in air, forming μ-oxo-bridged $[Fe^{III}(saloph)]_2O$. This same μ-oxo compound forms as a byproduct in the reaction of Fe^{II}(saloph) with 2,6-DtBQ in THF in the argon-atmosphere box. For comparison purposes we also prepared samples of the corresponding monoprotonated hydroquinone complexes Fe^{III}(saloph)(2,6-DtBHQ), where 2,6-DtBHQ is the monoanion of the hydroquinone, and Fe^{III}(saloph)(catH), where CatH is the monoanion of catechol. These complexes were prepared by a reaction scheme developed in the work of Heistand et al.[14] where the acetate complex Fe^{III}(saloph)(OAc) is reacted with a hydroquinone or catechol. Some μ-oxo dimer also forms in these reactions and is filtered off before the hydroquinone or catechol product is isolated. The complex Fe^{III}(saloph)(2,6-DtBHQ) is not as reactive in the air as Fe^{III}(saloph)(2,6-DtBSQ).

Table I. Mössbauer Parameters

compd	*T*, K	δ,[a] mm/s	ΔE_Q, mm/s	Γ,[b] mm/s	% area[c]
Fe^{II}(salpren)	5	0.91	2.70	0.53, 0.56	
Fe^{II}(saloph)[d]	77	1.27	2.43		
Fe^{II}(salprenOH)	80	0.46	0.83	0.29, 0.27	24.2
		1.06	2.52	0.17, 0.17	38.4
		1.11	3.21	0.20, 0.22	37.4
	5	0.15	1.01	1.75, 0.67	14.2
		1.06	2.79	0.47, 0.46	21.6
		1.13	3.20	1.45, 2.12	64.2
Fe^{II}(saldien)	5	0.99	2.39	0.35, 0.36	
$[Fe^{III}(salpren)]_2$(*p*-BHQ)	5	0.40	0.75	0.36, 0.36	
Fe^{III}(salpren)(3,5-DtBSQ)	5	0.41	0.71	0.43, 0.45	
Fe^{III}(salpren)(9,10-PhenSQ)	5	0.45	0.76	0.37, 0.37	
$[Fe^{III}(saloph)]_2$(*p*-BHQ)	19	0.36	0.89	0.19, 0.21	
Fe^{III}(saloph)(2,6-DtBHQ)	10	0.38	1.27	0.28, 0.34	
Fe^{III}(saloph)(2,6-DtBSQ)	5	0.35	0.67	0.66, 0.64	
Fe^{III}(saloph)(3,5-DtBSQ)	5	0.41	0.58	0.40, 0.41	
Fe^{III}(saloph)(9,10-PhenSQ)	5	0.45	0.44	0.68, 0.70	
$[Fe^{III}(salprenO)]_2$·THF	80	0.48	0.45	0.32, 0.28	
Fe^{II}(salprenOH)(acac)	80	1.14	2.44	0.23, 0.22	
$[Fe^{III}(saldien)]_2$(*p*-BHQ)	80	0.54	0.72	0.20, 0.22	

[a] Relative to iron metal. [b] Half-width at half-maximum, listed in order of increasing velocity of peak. [c] When there is more than one quadrupole-split doublet, the area percentage is given for each doublet. [d] See ref 17.

The complex Fe^{II}(salprenOH) reacts with *o*- and *p*-quinones over a period of about 3 h to yield hydroquinones and a new dimeric iron(III) species that crystallizes as a THF solvate, $[Fe^{III}(salprenO)]_2$·THF. The reaction of Fe^{II}(salprenOH) with acetylacetone gives a 1:1 ferrous acetylacetone adduct (cf. Mössbauer Spectroscopy). It was not possible to characterize any definite N_2 chelates from the reaction of Fe^{II}(salprenOH) and bidentate ligands such as *o*-phenylenediamine or 2,2′-bipyridine, even though other iron(II) neutral tetradentate complexes such as Fe^{II}(salen) or Fe^{II}(saloph) react with these same diamines to yield Fe^{II}(salen)(diamine) and Fe^{II}(saloph)(diamine).[16] These observations may be indicative of an interaction between the iron ion and the alcoholic oxygen atom in Fe^{II}(salprenOH). The unusual reaction of Fe^{II}(salprenOH) with acetylacetone wherein acetylacetone does not chelate the iron ion and oxidize the metal to iron(III), in spite of the ease of oxidation of Fe^{II}(salprenOH), must reflect either some steric hindrance in the complex or, more likely, an intermolecular or intramolecular interaction between the iron ion and the alcoholic oxygen atom which prevents Fe^{II}(salprenOH) from chelating a bidentate ligand. It was found that Fe^{II}(salprenOH) reacts with phenylisocyanate to give Fe^{II}(salprenOC(ONH(C_6H_5))), demonstrating the lability of the alcoholic proton.

Over a 1-week period the complex Fe^{II}(saldien) reacts with *p*-BQ to give the binuclear hydroquinone-bridged complex $[Fe^{III}(saldien)]_2$(*p*-BHQ). It did not prove possible to isolate

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[15] A crystal structure has just been determined for one of these complexes; see: Lauffer, R. B.; Heistand, R. H., II; Que, L., Jr. *Inorg. Chem.* **1983**, *22*, 50.

[16] (a) Tuchagues, J.-P. M., unpublished work. (b) Nakamura, M.; Itoh, T.; Okawa, H.; Kida, S. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2281.

a product from the reaction of Fe^{II}(saldien) with 2,6-DtBQ. A reaction seems to occur between Fe^{II}(saldien) and *o*-quinones; however, we were not able to isolate and characterize either a 1:1 metal-semiquinone complex or the 2:1 metal-hydroquinone dianion complex. Furthermore, the reaction between Fe^{II}(saldien) and bidentate ligands such as *o*-phenylenediamine or 2,2'-bipyridine did not lead to any characterizable mixed-ligand complex. Thus, Fe^{II}(saldien) behaves like a pentacoordinated N_3O_2 complex.

Mössbauer Spectroscopy. The parameters obtained from the least-squares fitting of the Mössbauer spectra for the compounds in this work are listed in Table I. The compounds Fe^{II}(salpren), Fe^{II}(saloph), Fe^{II}(saldien), and Fe^{II}(salprenOH)(Hacac) are each characterized by single quadrupole-split doublets with isomer shifts ranging from +0.91 to +1.14 mm/s vs. iron. These isomer shifts are well within the range expected for divalent iron, and the observed quadrupole-splitting parameters substantiate the high-spin nature of each ferrous ion.[17]

Three quadrupole-split doublets are present in the spectrum of Fe^{II}(salprenOH). This compound is very air sensitive. Spectra were run for two different samples, and as with all compounds in this study, the samples were loaded into a pressed-fit sample cell in the argon-atmosphere box and then transferred rapidly to the helium atmosphere of the spectrometer. The first sample was run at 80 K; one doublet with $\delta = 0.46$ mm/s (vs. iron) and $\Delta E_Q = 0.83$ mm/s clearly results from a high-spin ferric impurity with 24.2% of the spectral area. This ferric impurity is due to oxidation of the Fe^{II}(salprenOH) in the Mössbauer cell. In order to minimize this oxidation, the second sample was loaded into a cell in the box and this cell was then sealed with paraffin before it was removed. In this case the area of the ferric doublet was reduced to 14.2%. In addition to the ferric doublet, each of the above spectra show two high-spin ferrous doublets. Examination of the spectra for the two samples shows that the doublet with $\delta = 1.13$ mm/s and $\Delta E_Q = 3.20$ mm/s is attributable to the original Fe^{II}(salprenOH) complex; this doublet is more prevalent for the second sample in the paraffin-sealed cell. The second iron(II) doublet results from limited exposure of the Fe^{II}(salprenOH) sample to humid air. It is likely that either an H_2O molecule or an O_2 molecule binds to the iron ion in Fe^{II}(salprenOH) in the solid state. It should be noted, however, that Fe^{II}(salprenOH)(Hacac) from the reaction of acetylacetone and Fe^{III}(salprenOH) (all reactants maintained in the box) gives a single doublet in its Mössbauer spectrum.

There has been one other report of a high-spin iron(II) complex reacting in the solid state with humid air. Hodges et al.[18] reported that solid samples of [Fe(TMC)Br]Br, where TMC is tetramethylcyclam (1,4,7,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), and related compounds react with humid air. Two different iron(II) quadrupole-split doublets were seen for each compound. The relative ratios of the two doublets reflected the contact time with the humid air.

All of the semiquinone, catecholate, and hydroquinone complexes and [Fe^{III}(salprenO)]$_2$·THF give Mössbauer spectra with a single doublet. The isomer shifts range from 0.35 to 0.48 mm/s vs. iron, and this together with the magnitude of quadrupole splittings characterizes these compounds as high-spin iron(III) complexes.

The Mössbauer spectra for the *p*-semiquinone complex Fe^{III}(saloph)(2,6-DtBSQ) and the *p*-hydroquinone complex Fe^{III}(saloph)(2,6-DtBHQ) are appreciably different, which demonstrates that these two compounds are in fact different. The *p*-hydroquinone complex was prepared by reacting Fe^{III}(saloph)(OAc) with the hydroquinone, and it is clear tht the ligand in this complex has to be the monoprotonated hydroquinone dianion. The *p*-semiquinone complex shows one doublet with $\Delta E_Q = 0.670$ mm/s, whereas the quadrupole splitting (=1.27 mm/s) is almost twice as large for the *p*-hydroquinone complex. It is not readily possible to interpret this difference in quadrupole splitting. For comparison purposes, a sample of Fe^{III}(saloph)(CatH) was prepared, where CatH is the monoprotonated catecholate ligand. Heistand et al.[14] determined with an X-ray structure that the iron has a square-pyramidal coordination geometry with the catechol monoanion coordinated in a monodentate fashion in the axial site. A single doublet is seen at 11 K for Fe^{III}(saloph)(CatH) with $\Delta E_Q = 0.539$ mm/s and $\delta = 0.462$ mm/s. On the other hand, it was found tht Fe^{III}(saloph)(OAc) has one well-resolved doublet at 20 K with $\Delta E_Q = 1.484$ mm/s and $\delta = 0.295$ mm/s.

Infrared Spectroscopy. Infrared spectra were recorded for all compounds prepared as Nujol or Fluorolube mulls under an argon atmosphere.

The salprenOH ligand shows a strong and broad OH band centered at 3400 cm^{-1} due to both the phenolic O-H bonds and the secondary alcoholic function. The position and the broadness of the band are indicative of hydrogen bonding (probably between the phenolic protons and the imine nitrogen atoms). This OH band is reduced in intensity, moderately sharpened, and shifted down to ~3280 cm^{-1} for the Fe^{II}(salprenOH) complex. Since the phenolic protons are not present in the ferrous complex, the 3280-cm^{-1} OH band is attributable to the secondary alcoholic function. The ~120-cm^{-1} shift to lower energies is indicative of a strong inter- or intramolecular interaction between the alcoholic oxygen and the ferrous iron. This OH band is not further shifted on going from the Fe^{II}(salprenOH) compound to the Fe^{II}(salprenOH)(acac) complex (3275 cm^{-1}), indicating that there is no important modification in the Fe^{II}-OH interaction. On the other hand, as expected, the OH band disappeared for the dimeric compound [Fe^{III}(salprenO)]$_2$·THF.

While the saldien ligand shows a weak NH stretching band at 3330 cm^{-1}, the Fe^{II}(saldien) complex is characterized by a NH stretching frequency of 3290 cm^{-1} and the [Fe^{III}(saldien)]$_2$(*p*-BHQ) binuclear complex is characterized by a NH stretching frequency of 3200 cm^{-1}, indicating that the secondary amine nitrogen interacts with the iron in different ways in these two saldien complexes. The small decrease in the NH stretching frequency of Fe^{II}(saldien) is to be compared with the one observed by Taylor et al.[19] for Mn^{II}(saldien). On the other hand, the large decrease in the NH stretching frequency of [Fe^{III}(saldien)]$_2$(*p*-BHQ) is similar to those observed for hexacoordinated Mn(III) or pentacoordinated Mn(II) complexes of XSALDPT ligands.[19,20] This suggests a different degree of N(-H) coordination in Fe^{II}(saldien) and [Fe^{III}(saldien)]$_2$(*p*-BHQ) or a difference in structure. Fe^{II}(saldien) may be either a tetracoordinated monomeric compound as Ni^{II}(saldien)[21] or, more likely, because of its reactivity, a pentacoordinated dimeric complex as Cu^{II}(saldien).[22]

The fact that the *o*-quinone and *p*-quinone ligands are reduced in the 1:1 and 1:2 complexes is confirmed by the infrared spectra. Free quinones are characterized by strong C=O

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Table II. Effective Magnetic Moments (μ_B)

compd	*T*, K 285.5	103	4.2
Fe^{II}(salprenOH)	5.36	5.30	3.56
Fe^{II}(salprenOH)(acac)	4.75	4.72	3.67
Fe^{II}(saldien)	5.09	5.15	1.77
$[Fe^{III}(salpren)]_2$(*p*-BHQ)$\cdot{}^1/_2$THF	4.74	4.00	1.01
Fe^{III}(salpren)(3,5-DtBSQ)	4.94	4.67	3.78
Fe^{III}(salpren)(9,10-PhenSQ)	4.79	4.49	2.55
$[Fe^{III}(saloph)]_2$(*p*-BHQ)$\cdot{}^1/_2$THF	5.40	5.21	1.65
Fe^{III}(saloph)(2,6-DtBHQ)	5.55	5.30	3.63
Fe^{III}(saloph)(2,6-DtBSQ)	5.02	4.89	4.57
Fe^{III}(saloph)(3,5-DtBSQ)$\cdot{}^1/_2$THF	4.57	4.76	3.98
Fe^{III}(saloph)(9,10-PhenSQ)$\cdot$THF	4.58	4.98	4.42
$[Fe^{III}(saldien)]_2$(*p*-BHQ)$\cdot{}^1/_2$THF	5.60	5.25	1.79
$[Fe^{III}(salprenO)]_2\cdot$THF	5.11	4.35	0.30

stretching frequencies ranging from 1655 to 1700 cm^{-1}. No bands above 1640 cm^{-1} are observed for any of the quinone complexes isolated in this work, indicating that the quinones have been reduced. Unfortunately, direct assignment of a CO semiquinone stretching band or of a CO stretching band of the dianion of an hydroquinone is not possible because of the C=N imine and CH_2 bands of the ligands, even when the 1450-cm^{-1} band of Nujol was avoided by preparing the samples as Fluorolube mulls.

Magnetic Susceptibility Data. The magnetic susceptibility data obtained for the compounds described in this work are summarized in Table II. The detailed data are available in the supplementary material. The complexes Fe^{II}(salprenOH), Fe^{II}(salprenOH)(acac), and Fe^{II}(saldien) have effective magnetic moments decreasing from 5.36, 4.75, and 5.09 μ_B, respectively, at 285.5 K down to 3.56, 3.67, and 1.77 μ_B, respectively, at 4.2 K. Octahedral, high-spin d^6 systems are expected to have effective magnetic moments of ca. 5.5 μB at room temperature, but increasing electron delocalization and distortion from cubic symmetry cause the magnetic moments to approach the spin-only value and to vary little with temperature.[23] As in the case of Fe^{II}(salen)[24] or Fe^{II}(saloph),[25] the magnetic behavior of the iron(II) complexes of salprenOH and saldien is consistent with the fact that each complex has four unpaired electrons and suggests that they have distorted structures with considerable delocalization. In the case of Fe^{II}(salprenOH) and Fe^{II}(salprenOH)(Hacac) the moderate reduction in μ_{eff} with decreasing temperature may be due to intermolecular magnetic exchange interactions. However, the more pronounced decrease in the effective magnetic moment of Fe^{II}(saldien) with decreasing temperature, which is comparable to the reductions observed for the binuclear ferric complexes bridged by the dianions of hydroquinones, suggests a dimeric $[Fe^{II}(saldien)]_2$ complex with an intramolecular antiferromagnetic exchange interaction between two $S = 2$ ions. Support for this hypothesis can be drawn from the literature. Whereas the ligand saldpt resulting from the Schiff-base condensation between salicylaldehyde and bis(3-aminopropyl)amine affords monomeric pentacoordinated complexes with Mn(II), Co(II), Ni(II), Cu(II), and Zn(II),[19,20] the ligand saldien with its shorter ethylene linkages affords either monomeric tetracoordinated complexes (e.g. Ni(II)[21]) with one ligand atom dangling or dimeric pentacoordinated complexes. The latter type of saldien is represented by the structurally characterized Cu(II) complex,[22] where each Cu(II) ion is pentacoordinate with three donor atoms from one ligand and two from the other saldien ligand. This dimer structure is also postulated for Mn^{II}(saldien).[19] Figure 1 illustrates the variable-temperature magnetic susceptibility data for $[Fe^{II}(saldien)]_2$. These data were least-squares fit to the theoretical equation[26] for an isotropic magnetic exchange interaction between two $S_1 = S_2 = 2$ ions, by employing the $\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$ spin Hamiltonian. The solid lines in Figure 1 represent this fit, which can be seen to be good. Least-squares fitting parameters are summarized in Table III, where it can be seen that $J = -2.2$ cm^{-1} for $[Fe^{II}(saldien)]_2$.

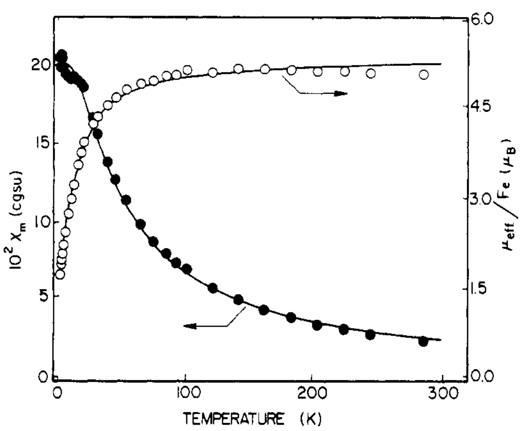

Figure 1. Variable-temperature magnetic susceptibility data for $[Fe^{II}(saldien)]_2$. The solid lines result from a least-squares fit of the data to the theoretical equation for isotropic magnetic exchange in a dimer with $S_1 = S_2 = 2$.

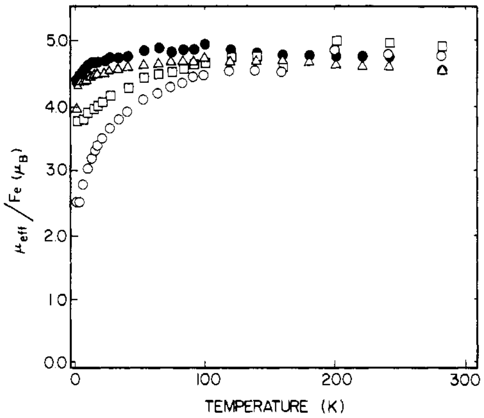

Figure 2. Effective magnetic moment (μ_{eff}) per molecule as a function of temperature: (□) Fe^{III}(salpren)(3,5-DtBSQ); (△) Fe^{III}(saloph)(3,5-DtBSQ)$\cdot{}^1/_2$THF; (●) Fe^{III}(saloph)(9,10-PhenSQ)$\cdot$THF; (○) Fe^{III}(salpren)(9,10-PhenSQ)$\cdot{}^1/_2$THF.

Table III. Magnetic Susceptibility Fitting Parameters

compd	*J*, cm^{-1}	g_{av}
$[Fe^{II}(saldien)]_2$	−2.2	2.23
$[Fe^{III}(salpren)]_2$*p*-BQ$\cdot{}^1/_2$THF	−6.7	1.90
$[Fe^{III}(saloph)]_2$*p*-BQ$\cdot{}^1/_2$THF	−2.2	1.90
$[Fe^{III}(saldien)]_2$*p*-BQ$\cdot{}^1/_2$THF	−3.4	1.93
$[Fe^{III}(salprenO)_2]\cdot$THF	−6.9	2.09

The *o*-semiquinone complexes Fe^{III}(salpren)(3,5-DtBSQ), Fe^{III}(salpren)(9,10-PhenSQ), Fe^{III}(saloph)(3,5-DtBSQ), and Fe^{III}(saloph)(9,10-PhenSQ) have effective magnetic moments per molecule of 4.94, 4.79, 4.57, and 4.58 μ_B, respectively, at 285.5 K and exhibit little temperature dependence in μ_{eff} down to liquid-nitrogen temperature (see Figure 2). As was found for the Fe^{III}(salen)(*o*-semiquinone) complexes,[10,27] the single

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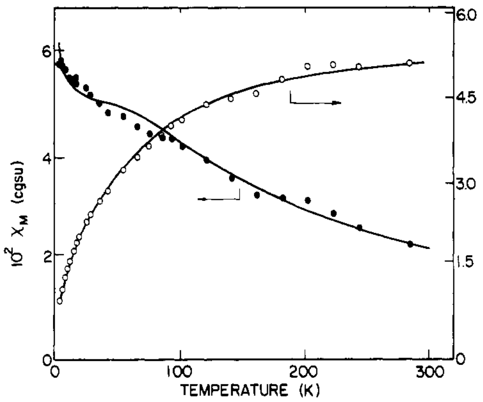

Figure 3. Variable-temperature magnetic susceptibility data for $[\mathrm{Fe^{III}(salpren)}]_2(p\text{-BHQ})\cdot{}^1/_2\mathrm{THF}$. The solid lines result from a least-squares fit of the data to the theoretical equation for isotropic magnetic exchange in a binuclear complex with $S_1 = S_2 = {}^5/_2$.

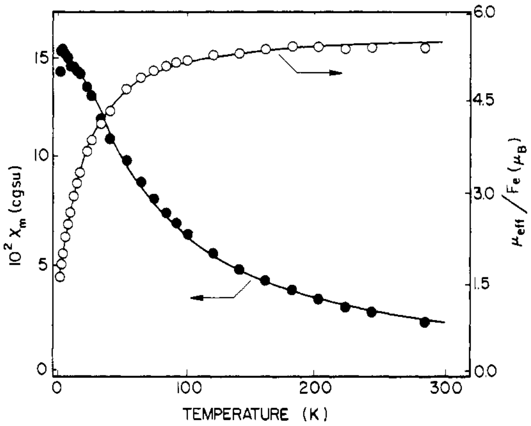

Figure 4. Variable-temperature magnetic susceptibility data for $[\mathrm{Fe^{III}(saloph)}]_2(p\text{-HBQ})\cdot{}^1/_2\mathrm{THF}$. The solid lines result from a least-squares fit of the data to the theoretical equation for isotropic magnetic exchange in a binuclear complex with $S_1 = S_2 = {}^5/_2$.

unpaired electron of the chelated *o*-semiquinone ligands in the above complexes is strongly antiferromagnetically coupled to the five unpaired electrons of the ferric ion to give an $S = 2$ ground state for each of the complexes. There is no evidence for thermal population of the $S = 3$ excited state at 285.5 K. This is in agreement with the work of Feher et al.,[5g] who conclude that the semiquinones in the primary electron-acceptor site of the photosynthetic electron-transport chain are not directly coordinated to the Fe(II) ion because the observed exchange interaction is very weak. The decrease in μ_{eff} seen for the two salpren complexes (see Figure 2) is attributable to *inter*molecular antiferromagnetic exchange interactions.

As illustrated in Figures 3–5, the three binuclear ferric complexes that are bridged by the hydroquinone dianion, $[\mathrm{Fe^{III}(saldien)}]_2(p\text{-BHQ})\cdot{}^1/_2\mathrm{THF}$, $[\mathrm{Fe^{III}(saloph)}]_2(p\text{-BHQ})\cdot{}^1/_2\mathrm{THF}$, and $[\mathrm{Fe^{III}(saldien)}]_2(p\text{-BHQ})\cdot{}^1/_2\mathrm{THF}$, exhibit similar susceptibility characteristics where μ_{eff}/Fe decrease from 4.74, 5.40, and 5.60 μ_B, respectively, at 285.5 K to 1.01, 1.65, and 1.79 μ_B at 4.2 K. The data for these three complexes were least-squares fit to the theoretical equations for an isotropic magnetic exchange interaction between two $S = {}^5/_2$ ions to give exchange parameters of $J = -6.7$, -2.2, and -3.4 cm^{-1}, respectively. These values are comparable to the exchange parameters reported for $[\mathrm{Fe^{III}(salen)}]_2(p\text{-BHQ})$ ($J = -2.5$ cm^{-1})[12] and $[\mathrm{Fe^{III}(TPP)}]_2(p\text{-BHQ})\cdot 2\mathrm{THF}$ ($J = -7.5$ cm^{-1}).[13]

Figure 6 illustrates the susceptibility data for $[\mathrm{Fe^{III}(salprenO)}]_2\cdot\mathrm{THF}$, the compound that results from the reaction of $\mathrm{Fe^{II}(salprenOH)}$ with either *o*-quinones or *p*-quinones. Fitting the data for this compound to the theoretical equation for magnetic exchange in an $S_1 = S_2 = {}^5/_2$ binuclear complex gives $J = -6.9$ cm^{-1}; the lines in Figure 6 correspond to this fit. A crystal structure is needed to ascertain the nature of the molecular association in this compound; however, it is clear that it is not a μ-oxo-bridged complex.

The magnetic susceptibility data observed for $\mathrm{Fe^{III}(saloph)(2,6\text{-}DtBSQ)}$ and $\mathrm{Fe^{III}(saloph)(2,6\text{-}DtBHQ)}$ (see Figure

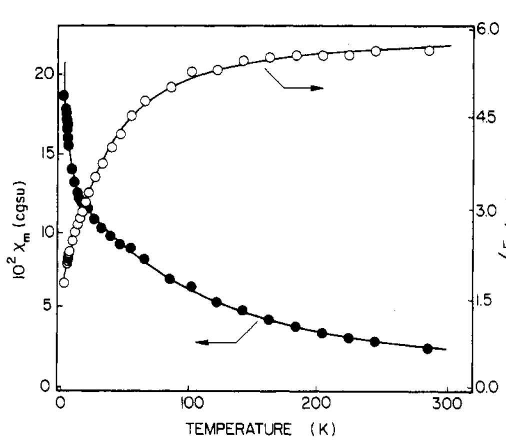

Figure 5. Variable-temperature magnetic susceptibility data for $[\mathrm{Fe^{III}(saldien)}]_2(p\text{-BHQ})\cdot{}^1/_2\mathrm{THF}$. The solid lines result from a least-squares fit of the data to the theoretical equation for isotropic magnetic exchange in a binuclear complex with $S_1 = S_2 = {}^5/_2$.

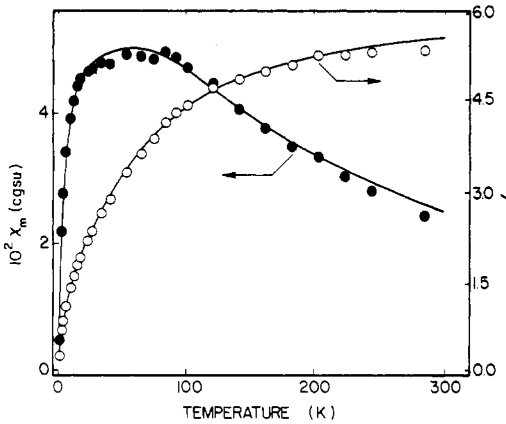

Figure 6. Variable-temperature magnetic susceptibility data for $[\mathrm{Fe^{III}(salprenO)}]_2\cdot\mathrm{THF}$. The solid lines result from a least-squares fit of the data to the theoretical equation for isotropic magnetic exchange in a binuclear complex with $S_1 = S_2 = {}^5/_2$.

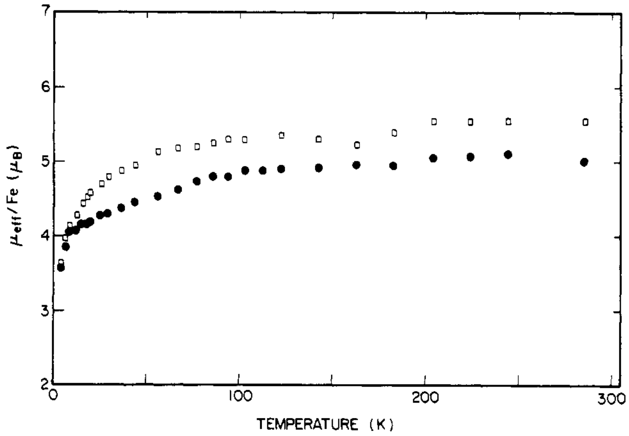

Figure 7. Effective magnetic moment (μ_{eff}) per molecule as a function of temperature: (□) $\mathrm{Fe^{III}(saloph)(2,6\text{-}DtBHQ)}$; (●) $\mathrm{Fe^{III}(saloph)(2,6\text{-}DtBSQ)}$.

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7) support the conclusion made from Mössbauer data that these two compounds are different. The *p*-semiquinone complex has an effective magnetic moment per molecule of 5.02 μ_B at 285.5 K, and there is little temperature dependence in μ_{eff} down to liquid-helium temperature (4.57 μ_B at 4.2 K). The 285.5 K value for μ_{eff} is consistent with the iron(III)–*p*-semiquinone formulation of this compound where there is a strong antiferromagnetic exchange interaction to given an $S = 2$ ground state. On the other hand, the hydroquinone compound Fe^{III}(saloph)(2,6-DtBHQ) has $\mu_{eff} = 5.55$ μ_B at 285.5 K. Compared to the case for the *p*-semiquinone complex, a larger decrease in μ_{eff} down to a value of 3.63 μ_B at 4.2 K is observed for the hydroquinone compound. The presence of a small amount of μ-oxo dimer in the hydroquinone sample apparently is the explanation for why the μ_{eff} value at 285.5 K is somewhat below the spin-only value of 5.9 μ_B expected for an $S = {}^5/_2$ species.

Summary and Comments. The complexes Fe^{II}(salpren) and Fe^{II}(saloph) react with 9,10-PhenQ, 3,5-DtBQ, and *p*-BQ in the same manner as found for Fe^{II}(salen).[10,12] The two *o*-quinones oxidatively add to the ferrous complex to give a hexacoordinate ferric complex with a chelated *o*-semiquinone complex. Binuclear ferric complexes bridged by the dianion of the hydroquinone result from the reactions with *p*-BQ.

Among the four ferrous compounds studied in this work, Fe^{II}(salprenOH) has not been previously described and Fe^{II}(saldien) only briefly.[28] In the case of the first complex it is unlikely that the salprenOH ligand coordinates as a N_2O_2 tetradentate ligand, as evidenced by the inability of Fe^{II}(salprenOH) to chelate diamines or acetylacetone. Perhaps the salprenOH ligand functions as a N_2O_3 pentadentate ligand, employing the alcoholic oxygen atom as a ligand site. More probable is the possibility that a dimeric structure is found for Fe^{II}(salprenOH). A crystal structure is needed to understand why the reaction of a quinone with Fe^{II}(salprenOH) only leads to the oxidation of the complex to give $[Fe^{III}(salprenoO)]_2$, which is characterized to have a weak antiferromagnetic exchange interaction.

The antiferromagnetic exchange interaction observed for Fe^{II}(saldien) points to a dimeric structure as found for Cu^{II}(saldien).[22] Each copper(II) ion has a trigonal-bipyramidal coordination geometry, utilizing three ligand atoms from one saldien and two ligands atoms from the second saldien. The inability of Fe^{II}(saldien) to chelate diamines and *o*-semiquinones is attributable to the dimeric structure. However, Fe^{II}(saldien) reacts with *p*-BQ to give "$[Fe^{III}(saldien)]_2$(*p*-HBQ)". Since Fe^{II}(saldien) probably has a dimeric structure, the ferric–hydroquinone product likely has a chain-type structure with $[Fe^{III}(saldien)]_2$ units bridged by the dianions of the hydroquinone.

The complex Fe^{III}(saloph)(2,6-DtBSQ) prepared in this work is the first iron complex reported to have a coordinated *p*-semiquinone ligand. The *p*-semiquinone form of biologically important quinones has been shown to be involved in magnetic exchange interactions with iron sites in proteins.

Experimental Section

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 4-Å sieves to minimize the water content. Schlenk apparatus was employed to prepare Fe^{II}(salpren), Fe^{II}(saloph), Fe^{II}(salprenOH), Fe^{II}[salprenOC(O)NHPh], and Fe^{II}(saldien). Reactions leading to the formation of the quinone adducts of the Schiff-base complexes were accomplished in a Vacuum Atmospheres Corp. Dri-Lab equipped with an H.E. 493 Dri-train.

Dimethylfomamide (DMF) used in the synthesis of Fe^{II}(salpren) and Fe^{II}(salprenOH) was shaken over KOH for 1 h, refluxed over BaO for 30 min, and fractionally distilled under argon. The center cut (10–90%) was further distilled in vacuo. Cyclohexane, toluene, benzene, and tetrahydrofuran (THF) 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 argon. Absolute ethanol was distilled under argon before use to remove trace mtal impurities. All solvents were degassed in vacuo.

Reagent grade salicylaldehyde, 1,3-diaminopropane, *o*-phenylenediamine, 1,3-diamino-2-hydroxypropane, diethylenetriamine, 2,4-pentanedione, and phenylisocyanate were purchased from Aldrich and used as received.

The quinones 3,5-DtBQ and 2,6-DtBQ were used without further purification. Samples of *p*-BQ were first sublimed and then recrystallized from tetrachloroethylene. Technical grade 9,10-PhenQ was purified via the bisulfite addition product.[29]

Fe^{II}(salpren). The salpren ligand was synthesized by condensation of salicylaldehyde and 1,3-diaminopropane in absolute ethanol. A sample of Fe^{II}(salpren) was prepared by reacting the salpren ligand with $Fe(CO)_5$, which had been freshly distilled and degassed under argon, in the manner described by Calderazzo for Fe^{II}(salen).[30] Fe^{II}(salpren) prepared in this manner was found to be analytically purer than Fe^{II}(salpren) synthesized from ferrous acetate and salpren in pure ethanol. Anal. Calcd for $C_{17}H_{16}N_2O_2Fe$: C, 60.74; H, 4.80; N, 8.33; Fe, 16.61. Found: C, 60.89; H, 5.10; N, 8.37; Fe, 16.48.

Fe^{II}(saloph). The saloph ligand was synthesized by condensation of salicyladehyde and *o*-phenylenediamine in absolute ethanol and recrystallized from CH_2Cl_2–hexane. Fe^{II}(saloph) was prepared as an ethanol solvate by reacting the saloph ligand with freshly prepared ferrous acetate in pure ethanol. In a typical preparation $Fe(C_2H_3O_2)_2{\cdot}4H_2O$ (2.46 g, 10.0 mmol) was placed in a 250-mL Schlenk flask and then 150 mL of deaerated pure ethanol was added. The slurry was stirred, and 3.20 g (10.0 mmol) of saloph was slowly added from a powder-addition tube. A dark olive-green product precipitated immediately. This slurry was refluxed and stirred for 36 h. The dark olive-green product was filtered, washed twice with 10-mL portions of deaerated pure ethanol, washed twice with 10-mL portions of deaerated pure methanol, and finally dried in vacuo for 4 h. Fe^{II}(saloph) was isolated as an EtOH solvate. Anal. Calcd for $C_{22}H_{20}N_2O_3Fe$: C, 63.48; H, 4.84; N, 6.72; Fe, 13.42. Found: C, 63.37; H, 4.72; N, 6.63; Fe, 13.41.

Fe^{II}(salprenOH). The salprenOH ligand was synthesized by condensation of salicylaldehyde and 1,3-diamino-2-hydroxypropane as described by Dey[31] Fe^{II}(salprenOH) was prepared either by reacting the salprenOH ligand with $Fe(CO)_5$, which had been freshly distilled and degassed with argon, in the manner described by Calderazzo[30] for Fe^{II}(salen) or by reacting ferrous acetate tetrahydrate with the ligand in pure ethanol in the manner described for Fe^{II}(saloph) (vide supra). The Fe^{II}(salprenOH) prepared from ferrous acetate was then suspended in distilled and degassed H_2O, stirred 12 h, filtered, and finally dried in vacuo at 120 °C for 6 h. Fe^{II}(salprenOH) was obtained as a red-purple powder. Anal. Calcd for $C_{17}H_{16}N_2O_3Fe$: C, 57.98; H, 4.58; N, 7.95; Fe, 15.86. Found: C, 57.42; H, 4.42; N, 7.50; Fe, 15.30.

Fe^{II}(saldien). The saldien ligand prepared from diethylenetriamine and salicylaldehyde in ethanol could not be isolated as a solid (orange oil). The Fe^{II}(saldien) complex was prepared through the template reaction of diethylenetriamine, salicylaldehyde, and ferrous acetate in pure degassed ethanol. In a typical preparation $Fe(C_2H_3O_2)_2{\cdot}4H_2O$ (2.46 g, 10.0 mmol) was placed in a 250-mL Schlenk flask and 100 mL of deaerated pure ethanol was added. The slurry was stirred and degassed. Salicylaldehyde (3.15 mL, 30 mmol) was slowly added, and a purple product precipitated immediately. Degassed diethylenetriamine (1.62 mL, 15 mmol) was slowly added to the purple slurry while it was stirred. The slurry turned dark red. The reaction mixture was refluxed and stirred for 36 h. The dark red product was filtered, washed twice with 10-mL portions of deaerated pure ethanol, washed twice with 10-mL portions of degassed pure methanol, and finally dried in vacuo for 4 h. Anal. Calcd for $C_{18}H_{19}N_3O_2Fe$: C, 59.20; H, 5.24; N, 11.51; Fe, 15.29. Found: C, 58.22; H, 5.23; N, 11.52; Fe, 14.96.

$[Fe^{III}(salpren)]_2$(*p*-BHQ). Fe^{II}(salpren) (0.34 g, 1 mmol) was

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suspended in THF (15 mL) and stirred. The quinone *p*-BQ (0.11 g, 1 mmol) was dissolved in THF (10 mL). The *p*-BQ solution was slowly added to the Fe^{II}(salpren) slurry. The color turned quickly to brown and more slowly to black-brown. The reaction mixture was stirred 60 h, during which half of the THF was very slowly evaporated. The black-brown resulting slurry was filtered. The black microcrystals were washed twice with 5-mL portions of THF and dried in vacuo for 4 h. Anal. Calcd for $C_{40}H_{36}N_4O_6Fe_2\cdot{}^1/_2THF$: C, 61.78; H, 4.94; N, 6.86; Fe, 13.68. Found: C, 61.60; H, 5.11; N, 6.65; Fe, 13.14.

Fe^{III}(salpren)(9,10-PhenSQ). This reaction was carried out in the same manner as for $[Fe^{III}$(salpren)$]_2$(*p*-BHQ) except that the reaction mixture was stirred only 36 h. The complex was obtained as dark green reddish microcrystals of Fe(salpren)(9,10-phenSQ)$\cdot{}^1/_2$THF. Anal. Calcd for $C_{33}H_{28}N_2O_{4.5}Fe$: C, 68.29; H, 4.86; N, 4.83; Fe, 9.62. Found: C, 68.00; H, 4.86; N, 4.88; Fe, 9.30.

Fe^{III}(salpren)(3,5-DtBSQ). This reaction was carried out in the same manner. The reaction mixture was a black solution even after evaporation of more than half of the THF. Heptane (10 mL) was added, and the black product that precipitated was filtered, washed twice with 5-mL portions of heptane, and dried in vacuo for 5 h. Anal. Calcd for $C_{31}H_{36}N_2O_4Fe$: C, 66.91; H, 6.52; N, 5.02; Fe, 10.04. Found: C, 66.20; H, 6.50; N, 5.24; Fe, 9.90.

$[Fe^{III}$(saloph)$]_2$(*p*-BHQ). Fe^{II}(saloph)(EtOH) (0.42 g, 1 mmol) was dissolved in THF (20 mL), and the resulting green-olive solution was filtered. The quinone *p*-BQ (0.11 g, 1 mmol) was dissolved in THF (10 mL). The light yellow *p*-BQ solution was slowly added to the stirred Fe^{II}(saloph) solution. A black product precipitated immediately. The black slurry was stirred for 36 h. The black product was filtered, washed twice with 5-mL portions of THF, and finally dried in vacuo for 4 h. Anal. Calcd for $C_{46}H_{32}N_4O_6Fe_2\cdot{}^1/_2THF$: C, 65.18; H, 4.10; N, 6.33; Fe, 12.63. Found: C, 64.69; H, 3.98; N, 6.25; Fe, 12.26.

Fe^{III}(saloph)(2,6-DtBSQ). Fe^{II}(saloph)(EtOH) (0.42 g, 1 mmol) was dissolved in THF, and the resulting green-olive solution was filtered. The quinone 2,6-DtBQ (0.22 g, 1 mmol) was dissolved in THF (10 mL). The 2,6-DtBQ solution was slowly added to the stirred Fe^{II}(saloph) solution without color change or precipitation. The reaction mixture was stirred for 36 h and then filtered. Heptane (20 mL) was added to the dark-green filtrate. The dark-green product that precipitated was filtered, washed twice with 5-mL portions of heptane, and dried in vacuo for 5 h. Anal. Calcd for $C_{34}H_{34}N_2O_4Fe$: C, 69.16; H, 5.80; N, 4.74; Fe, 9.46. Found: C, 68.62; H, 5.83; N, 4.91; Fe, 9.57.

Fe^{III}(saloph)(9,10-PhenSQ). This reaction was carried out in the same manner as for $[Fe^{III}$(saloph)$]_2$(*p*-BHQ). Immediate precipitation did not occur, but the solution turned to dark green. The reaction mixture was stirred for 36 h. The resulting black-green slurry was filtered. The black-green product was washed with THF (5 mL) and heptane (10 mL) and finally dried in vacuo for 5 h. Anal. Calcd for $C_{34}H_{22}N_2O_4Fe.THF$: C, 70.16; H, 4.65; N, 4.31; Fe, 8.59. Found: C, 69.73; H, 4.61; N, 4.33; Fe, 8.37.

Fe^{III}(saloph)(3,5-DtBSQ). This reaction was carried out in the same manner as for Fe^{III}(saloph)(2,6-DtBSQ). The complex was obtained as a dark green powder. Anal. Calcd for $C_{34}H_{34}N_2O_4Fe\cdot{}^1/_2THF$: C, 69.01; H, 6.11; N, 4.47; Fe, 8.91. Found: C, 69.00; H, 6.12; N, 4.49; Fe, 8.56.

$[Fe^{III}$(salprenO)$]_2\cdot$THF. Fe^{II}(salprenOH) (0.36 g, 1 mmol) was dissolved in THF (10 mL), and the resulting red-purple solution was filtered. The quinone *p*-BQ (0.11 g, 1 mmol) was dissolved in THF (10 mL). The *p*-BQ solution was slowly added to the stirred Fe^{II}(salprenOH) solution. The solution turned immediately to brown. A light brown solid began to precipitate from this solution 30 min later. The reaction mixture was left to stand for 24 h. The light brown product was filtered, washed twice with 10-mL portions of heptane, and dried in vacuo for 5 h. The same product was prepared in the same manner from Fe^{II}(salprenOH) and 3,5-DtBQ. Anal. Calcd for $C_{34}H_{30}N_4O_6Fe_2\cdot THF$: C, 58.94; H, 4.95; N, 7.23; Fe, 14.42. Found: C, 58.42; H, 4.85; N, 7.17; Fe, 14.53.

Fe^{II}(salprenOH)(Hacac). Fe^{II}(salprenOH) (0.36 g, 1 mmol) was dissolved in THF (30 mL), and the resulting red-purple solution was filtered. Acetylacetone (0.1 mL, 1 mmol) was slowly added to the stirred Fe^{II}(salprenOH) solution. The solution turned slowly from red-purple to red-brown (over 2–3 h). The reaction was allowed to stand for 5 weeks in the argon box. At that time the solution had completely turned brown and a brown solid had precipitated. The brown solid was filtered, washed twice with 10-mL portions of heptane, and dried in vacuo for 5 h. The complex was obtained as a brown powder. Anal. Calcd for $C_{22}H_{24}N_2O_5Fe$: C, 58.42; H, 5.35; N, 6.19; Fe, 12.35. Found: C, 57.81; H, 5.10; N, 6.16; Fe, 12.46.

Fe^{II}(salprenOC(O)NHPh). Fe^{II}(salprenOH) (0.36 g, 1 mmol) was dissolved in THF (50 mL) with stirring. To the resulting red-purple slurry was added phenylisocyanate (0.21 mL, 2×10^{-3} mol). The reaction mixture was refluxed and stirred over 48 h. Half of the THF was removed in vacuo. Heptane (30 mL) was added, yielding a light red-brown solid. The solid was filtered, washed twice with 10-mL portions of heptane, and dried in vacuo for 5 h. The complex was obtained as a light red-brown powder. Anal. Calcd for $C_{24}H_{21}N_3O_4Fe$: C, 61.16; H, 4.49; N, 8.92; Fe, 11.85. Found: C, 59.60; H, 4.69; N, 8.72; Fe, 11.06.

$[Fe^{III}$(saldien)$]_2$(*p*-BHQ). Fe^{II}(saldien) (0.185 g, 0.5 mmol) was suspended in THF (10 mL). The quinone *p*-BQ (0.06 g, $\sim 5 \times 10^{-4}$ mol) was dissolved in THF (5 mL). The *p*-BQ solution was slowly added to the stirred Fe^{II}(saldien) slurry without color change. The reaction mixture was stirred for 24 h and allowed to stand for 7 days to complete the reaction. At this point the red Fe^{II}(saldien) was consumed and the solution was dark brown. Half of the solution was removed in vacuo, affording a dark brown slurry. The slurry was filtered. The dark green precipitate obtained was washed twice with 5-mL portions of heptane and dried in vacuo for 5 h. Anal. Calcd for $C_{42}H_{42}N_6O_6Fe_2\cdot{}^1/_2THF$: C, 60.43; H, 5.30; N, 9.61; Fe, 12.77. Found: C, 59.97; H, 5.17; N, 9.49; Fe, 12.62.

2,6-DtBHQ. A sample of this hydroquinone was prepared from 2,6-DtBQ. The preparation used was a modification of the method described by Fieser et al.[32] for durohydroquinone. After reduction of the quinone with an acidic solution of stannous chloride, the hydroquinone was extracted from the aqueous phase with methylene chloride. The CH_2Cl_2 solution was then dried with magnesium sulfate. The CH_2Cl_2 was evaporated with a rotary evaporator, and then the hydroquinone was sublimed twice (mp 88–90 °C).

Fe(saloph)(CatH). This compound was prepared from Fe^{III}(saloph)(OAc)[33] in a modification of the method used by Heistand et al.[14] The reaction was carried out in the argon box with use of acetonitrile as solvent. Catechol was reacted as a solid with a hot acetonitrile solution of Fe^{III}(saloph)(OAc). Upon cooling of the reaction mixture, the catecholate complex was obtained in the form of dark brown to black microcrystals. These were filtered off, washed three times with 10-mL portions of pentane, and finally dried in vacuo for 5 h. Anal. Calcd for $C_{16}H_{19}N_2O_4Fe$: C, 65.16; H, 4.00; N, 5.84; Fe, 11.65. Found: C, 65.09; H, 3.92; N, 5.84; Fe, 11.67.

Fe(saloph)(2,6-DtBHQ). Fe^{III}(saloph)(OAc) (0.43 g, 1 mmol) was dissolved in 150 mL of boiling acetonitrile with stirring. The red μ-oxo dimer that formed was filtered off, and 2,6-DtBHQ (0.66 g, 3 mmol) was added as a solid to the hot acetonitrile solution of Fe^{III}(saloph)(OAc). The hydroquinone dissolved immediately, and the color of the reaction mixture changed slowly from brown to green. No crystallization or precipitation occurred on slow cooling of the reaction mixture over a period of 5 h. The reaction mixture was then taken to dryness. The dark green residue was crushed and washed several times with 10-mL portions of pentane in order to eliminate the excess hydroquinone. Because the acetate and hydroquinone complexes are soluble in the same solvents, we were not able to eliminate the few percent of unreacted acetate complex mixed with the hydroquinone complex. The resulting green powder was finally dried in vacuo for 5 h. Anal. Calcd for $C_{34}H_{35}N_2O_4Fe$: C, 69.03; H, 5.96; N, 4.74; Fe, 9.44. Found: C, 65.27; H, 5.29; N, 5.07; Fe, 9.69.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer. Samples were run as Nujol or Fluorolube mulls, prepared under argon and pressed between KBr plates.

Variable-temperature (4.2–285.5 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. Least-squares computer fittings of the magnetic susceptibility data were accomplished with an adapted version of the function-minimization program known as STEPT.[34]

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Iron-57 Mössbauer spectra were collected on a constant-acceleration spectrometer. Computer fitting of ^{57}Fe Mössbauer data to Lorentzian lines was carried out with a modified version of a previously reported program.[35]

Elemental analyses were carried out at the School of Chemical Sciences Microanalytical Laboratory, University of Illinois.

Acknowledgment. We are grateful for support from National Institutes of Health Grant HL 13652. J.-P.M.T. is grateful for support from a NATO postdoctoral fellowship. Mark Timken is to be thanked for help in fitting the magnetic susceptibility data and obtaining the Mössbauer spectra.

Registry No. Fe^{II}(salpren), 55095-98-2; Fe^{II}(saloph), 16828-80-1; Fe^{II}(salprenOH), 86471-94-5; Fe^{II}(saldien), 86471-95-6; [Fe^{III}(salpren)]$_2$(*p*-BHQ), 86471-96-7; Fe^{III}(salpren)(9,10-phenSQ), 86471-97-8; Fe^{III}(salpren)(3,5-DtBSQ), 86471-98-9; [Fe^{III}(saloph)]$_2$(*p*-BHQ), 86471-99-0; Fe^{III}(saloph)(2,6-DtBSQ), 86472-00-6; Fe^{III}(saloph)(9,10-phenSQ), 86472-01-7; Fe^{III}(saloph)(3,5-DtBSQ), 86472-02-8; [Fe^{III}(salprenO)]$_2$, 86480-34-4; Fe^{II}(salprenOH)(Hacac), 86472-03-9; Fe^{II}(salprenOC(O)NHPh), 86472-04-0; [Fe^{III}(saldien)]$_2$(*p*-BHQ), 86472-05-1; Fe(saloph)(CatH), 80041-63-0; Fe(saloph)(2,6-DtBHQ), 86507-79-1; 2,6-DtBHQ, 2444-28-2.

Supplementary Material Available: Tables IV–XVI, experimental and calculated magnetic susceptibility data (17 pages). Ordering information is given on any current masthead page.

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Studies on Complexes Containing Mixed-Valence Semiquinone–Catecholate Ligands. Synthesis and Characterization of Bis(*o*-quinone)(bipyridine)chromium(III) Complexes

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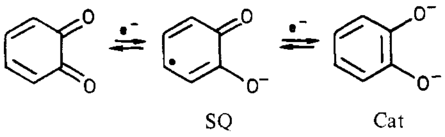
Received February 3, 1983

The synthesis of bis(*o*-quinone)(bipyridine)chromium complexes has been carried out by treating $Cr(bpy)(CO)_4$ with 3,5-di-*tert*-butyl-1,2-benzoquinone, tetrachloro-1,2-benzoquinone, or 9,10-phenanthrenequinone. The neutral complexes have two unpaired electrons and undergo one-electron oxidations and reductions by either chemical or electrochemical means. EPR studies on the $S = {}^1/_2$ cationic complexes indicate electronic ground states with spin density concentrated on the metal ions. The anionic complexes appear to be normal complexes of Cr^{3+}. Formulations for the members of the redox series based on their physical properties are $Cr(SQ)_2(bpy)^+$,Cr(SQ)(Cat)(bpy), and $Cr(Cat)_2(bpy)^-$. In each form the metal ion is trivalent, and redox activity involves changes in charge of the quinone ligands rather than the chromium ion.

Introduction

The coordination chemistry of *o*-quinone ligands, primarily catechols, has been a subject of interest since the beginning of the century, but only within the past decade have detailed studies been carried out on the composition and properties of quinone complexes.[1] One particularly interesting feature of these compounds is their redox chemistry. This interest has led to the development of compounds that show multielectron redox series facilitated by the electrochemical activity of ligands rather than the metal ion.[2] Problems with complex decomposition due to metal ion lability or reactivity are avoided in such a system.

Free *o*-quinones exist as catecholates, *o*-semiquinones, and *o*-benzoquinones, related by the addition or removal of charge (eq 1). Electrochemical interconversion of these forms can



(1)

occur by either one- or two-electron processes.[3] In principle, a complex containing quinone ligands can undergo two electron-transfer steps per quinone. The neutral tris(*o*-semiquinone)chromium(III), $Cr(SQ)_3$, complexes undergo both oxidation and reduction reactions through a sequence of species (eq 2) containing mixed-charge ligands bonded to Cr(III).[2]

$$Cr(BQ)_3{}^{3+} \overset{3e^-}{\rightleftharpoons} Cr(SQ)_3 \overset{3e^-}{\rightleftharpoons} Cr(Cat)^{3-} \qquad (2)$$

The metal ion is kinetically stable and not directly involved in the redox activity, and not until the ligands are in a fully oxidized BQ form does dissociation become a factor. In contrast, the $M_4(3,5\text{-DBSQ})_8$ (M = Mn, Co, Ni) molecules,[4,5] which have potential for showing a large number of redox steps, show only one or two reversible couples due to dissociation of the complex in solution. Members of the chromium series with mixed-charge ligands are related in an inverse sense to the class of complexes with mixed-valent metal ions joined by a ligand bridge. As such, there are metal ion bridges between mixed-charge ligands supporting interaction between ligands. When interligand coupling is strong, a delocalized ground state or class III behavior in the Robin and Day[6] sense results. Examples of this are found among the neutral bis and tris 1,2-dithiolene and diimine complexes.[7] A compound that shows localized mixed-charge ligands similar to the intermediate members of the chromium series is the cobalt complex Co(3,5-DBCat)(3,5-DBSQ)(bpy).[8] This compound has a localized electronic structure in solid state but in solution exists in equilibrium with a Co(II) form related by ligand-to-metal electron transfer (eq 3). Closely related is the P(V) compound

$$\underset{\textstyle I}{Co^{III}(3,5\text{-DBCat})(3,5\text{-DBSQ})(bpy)} \rightleftarrows Co^{II}(3,5\text{-DBSQ})_2(bpy) \qquad (3)$$

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