same argument explains the weaker interaction exhibited by $[Cu_2(dpt)_2(BiIm)](BPh_4)_2{\cdot}2CH_3CN$ where $J = -1.9$ cm^{-1} compared with $[Cu_2(dpt)_2(Ox)](BPh_4)_2$ where $J = -5.7$ cm^{-1}.

Finally, it should be pointed out that the $BiIm^{2-}$ bridge is most likely not totally equivalent to two Im^- bridges. The relatively short C(2)–C(2′) distances noted in $M_2(COD)_2(BiIm)$[13] and $M_4(CO)_8(BiIm)_2$[14] indicate the presence of some conjugation between the two imidazolate moieties in $BiIm^{2-}$. CNDO/2 calculations on $BiIm^{2-}$ do show considerable π-orbital interactions and also small changes in the σ framework. X-ray structural work is in progress on $[Cu_2(Me_5dien)_2(BiIm)](BPh_4)_2$.[41]

Acknowledgment. We are grateful for partial funding from National Institutes of Health Grant HL 13652. Thanks are also in order for Professor S. J. Lippard for telling us of his work on $[Cu_2(tren)_2(Im)]X_3$ complexes in advance of publication. We are also appreciative of samples of biimidazole and bibenzimidazole given to us by Dr. B. Fieselmann.

Registry No. $[Cu_2(tren)_2(Im)](PF_6)_3$, 66900-41-2; $[Cu_2(tren)_2(Im)](ClO_4)_3$, 66900-40-1; $[Cu_2(tren)_2(Im)](BPh_4)_2(ClO_4)$, 66842-05-5; $[Cu_2(tren)_2(BzIm)](ClO_4)_3$, 66842-03-3; $[Cu_2(tren)_2(2\text{-}MeIm)](PF_6)_3$, 66900-39-8; $[Cu_2(tren)_2(2\text{-}MeIm)](ClO_4)_3$, 66842-01-1; $[Cu_2(bpy)_4(Im)](PF_6)_3$, 66810-44-4; $[Cu_2(phen)_4(Im)](ClO_4)_3$, 66810-46-6; $[Cu_2(tren)_2(BiIm)](BPh_4)_2$, 66842-07-7; $[Ni_2(tren)_2(BiIm)](BPh_4)_2$, 66842-09-9; $[Cu_2(dpt)_2(BiIm)](BPh_4)_2$, 66810-48-8; $[Cu_2(Me_5dien)_2(BiIm)](BPh_4)_2$, 66810-56-8; $[Cu_2(dien)_2(BiIm)](BPh_4)_2$, 66810-54-6; $[Cu_2(Me_5dien)_2(BiBzIm)](BPh_4)_2$, 66810-52-4; $[Cu_2(dien)_2(BiBzIm)](BPh_4)_2$, 66810-50-2.

Supplementary Material Available: Tables I (analytical data) and II–XVI (calculated and observed magnetic susceptibility data (28 pages). Ordering information is given on any current masthead page.

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Magnetic Exchange Interactions in Binuclear Transition-Metal Complexes. 16. Binuclear Ferric Complexes from the Reaction of Fe^{II}(salen) with *p*-Quinones[1]

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The molecule Fe^{II}(salen) reacts with *p*-quinones (four different 1,4-benzoquinones, 1,4-naphthoquinone, and bianthrone) to give a compound with the composition $[Fe(salen)]_2Q$, where Q is the quinone moiety. It is shown with IR, variable-temperature magnetic susceptibility, EPR, and ^{57}Fe Mössbauer measurements that the compounds consist of high-spin ferric ions bridged by the dianion of a hydroquinone. *Intra*molecular antiferromagnetic exchange interactions are present in these binuclear iron(III) complexes, where the exchange parameter varies from -5.8 to -0.21 cm^{-1}. Several of the complexes exhibit asymmetric quadrupole-split doublets in their ^{57}Fe Mössbauer spectra. The asymmetries are found to be temperature dependent with a relatively symmetric doublet seen at low temperatures. Only two of the compounds give EPR signals, consisting of broad isotropic derivatives at $g =$ ca. 2.0.

Introduction

In photosynthesis and respiration, energy in the form of a redox potential gradient is transduced into metabolically useful energy. A series of coupled redox reactions, frequently referred to as an electron transport chain, is utilized to discharge this gradient and synthesize adenosine triphosphate (ATP) from adenosine diphosphate (ADP) and inorganic phosphate. Several types of lipid-soluble quinones have been found to be

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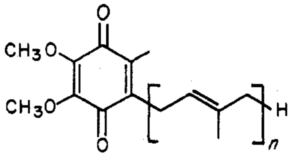
associated with electron-transport systems in plants, animals, and bacteria. *p*-Benzoquinones and 1,4-naphthoquinones are included among the biologically important quinones.[3,4]

Respiration in eucaryotes involves the *p*-benzoquinone known as ubiquinone which has the following structural characteristics:

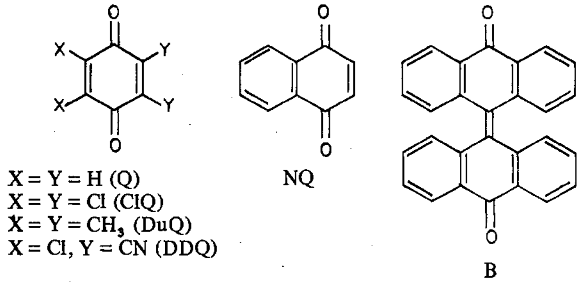


ubiquinone-*n*

In vertebrates, it is possible that the function of ubiquinone-10 is to transport electrons as a semiquinone between the various flavoprotein dehydrogenases and the collection of cytochromes and nonheme iron–sulfur proteins which accomplish the eventual reduction of oxygen. On the other hand, recent work[5,6] has indicated that ubiquinone-10 could function as a conformational altering activator of succinate dehydrogenase; in this case the compound is indicated to be in the totally reduced form of ubihydroquinone. There have been a few interesting observations and comments relative to the possible interaction of ubiquinone-10 with nonheme iron–sulfur proteins. For example, in their recent studies of EPR signals from beef heart tissues and mitochondria, Beinert et al.[7] observed an interesting EPR pattern at a g value of ca. 2.0. The pattern consisted of two broad signals with a magnetic field-independent separation of 82 G. It was assigned to a ubisemiquinone and a second paramagnetic species which were involved in either a dipole–dipole or magnetic exchange interaction. Moore and Folkers in earlier work[8] had shown that the reaction of ubiquinone-10 with ferric chloride and L-ascorbic acid in glacial acetic acid gave the 6-chromanol cyclization product from ubiquinone. From these observations they speculated that in the electron-transport chain some nonheme Fe(III) ion center binds the quinone in a η^4 π fashion. It was further suggested that an inorganic phosphate also binds to the Fe(III) ion followed by an *intra*molecular reaction to produce an "active phosphate" form of ubiquinone, thereby coupling the electron-transport process to the conversion of ADP to ATP. In summary, an examination of the literature shows that very little is known about the molecular and electronic structure of iron–quinone complexes.

In fact, relatively few transition-metal complexes with quinones have been reported.[9] *p*-Benzoquinones with relatively low reduction potentials, e.g., 1,4-benzoquinone and 2,3,5,6-tetramethyl-1,4-benzoquinone (DuQ = duroquinone), may function as η^2 two-electron and η^4 four-electron donating ligands. The complexes $[(Ph_3P)_2Pt](DuQ)$,[10] $[(Ph_3P)_2Ni]_2(DuQ)$,[11] and $(\eta^5\text{-}C_5H_5)M(DuQ)$,[12,13] where M = Co, Rh, or Ir, do exhibit this type of coordination. Some binuclear complexes have also been prepared. Recently, the synthesis and characterization of binuclear complexes of Ni(II) and Cu(II) bridged by the dianions of various 2,5-dihydroxy-1,4-benzoquinones were reported.[14] Pentacyanocobaltate anion and *p*-benzoquinone react to give the species $[(CN)_5Co(OC_6H_4O)Co(CN)_5]^{6-}$ where the dianion of the hydroquinone is bridging between two cobalt(III) ions.[15]

In the work presented in this paper our attention was drawn to some results reported by Floriani et al.[16] They reacted a series of *p*-benzoquinones with Co(II)– and Fe(II)–salen compounds to yield binuclear complexes with the composition $[(salen)M]_2Q$, where Q is the quinone moiety. It was suggested that the metal ions are oxidized to M(III) and that the bridge Q is the dianion of the hydroquinone. A further characterization of these iron compounds employing magnetic susceptibility measurements to 4.2 K, EPR, and ^{57}Fe Mössbauer determinations was deemed very useful in view of the paucity of data on iron complexes incorporating quinone ligands. Data are presented in this paper for the binuclear complexes resulting from the reaction of 2 mol of Fe^{II}(salen) with one of the following quinones.



X = Y = H (Q)
X = Y = Cl (ClQ)
X = Y = CH_3 (DuQ)
X = Cl, Y = CN (DDQ)

NQ

B

Experimental Section

Compound Preparation. All manipulations directed toward the isolation of product were carried out under an argon atmosphere in Schlenk-type apparatus. Solvents were purified by standard literature procedures and then degassed by refluxing under argon. The compound *N,N'*-ethylenebis(salicylideniminato)iron(II) was prepared as described previously.[17] 2,3,5,6-Tetramethylbenzoquinone (duroquinone), *p*-benzoquinone, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), and bianthrone (B) were purchased from Aldrich. Reagent grade duroquinone and DDQ were used without further purification. Bianthrone was recrystallized from tetrahydrofuran. *p*-Benzoquinone was first sublimed and then recrystallized from tetrachloroethylene. Practical grade 2,3,5,6-tetrachlorobenzoquinone (*p*-chloranil) and 1,4-naphthoquinone were purchased from Eastman, sublimed twice, and recrystallized from benzene.

Samples of $[(salen)Fe]_2Q$, where Q is the quinone moiety, were essentially prepared by the method of Floriani et al.[16] All reactions were carried out in Schlenk vessels, employing an argon atmosphere. This is necessary in order to avoid the formation of μ-oxo-bridged ferric complexes. A slight excess of the desired quinone was dissolved in THF, to which the appropriate amount of Fe(salen) was added. After stirring of the reaction mixture under argon for 48 h, the compounds were filtered and washed with THF. Due to the low solubility of bianthrone, this quinone was simply suspended in the reaction without complete dissolution. Analyses were performed in the School of Chemical Sciences' microanalytical laboratory; all analytical data are collected in Table I.[18]

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer. Samples were run as Nujol mulls, prepared under a nitrogen atmosphere and pressed between NaCl 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.[19]

Iron-57 Mössbauer spectra for samples at 4.2 K were obtained on an instrument previously described.[20] Liquid nitrogen and room temperature spectra were obtained with a second instrument.[21] Computer fitting of ^{57}Fe Mössbauer data to Lorentzian lines was carried out with a modified version of a previously reported program.[22]

Electron paramagnetic resonance (EPR) spectra were recorded on Varian E-9 X-band and E-15 Q-band spectrometers. Low-temperature spectra were obtained on the X-band unit with an Air Products Heli-tran liquid-helium cooling system. A carbon resistor sensing element was used to determine the temperatures.

Results

In agreement with Floriani et al.,[16] it was found that the reaction of 1 mol of various *p*-quinones with 2 mol of Fe^{II}(salen) gives a compound with the composition "$[Fe(salen)]_2$(quinone)". The analytical data for the compounds prepared in this work are given in Table I.[18] The *p*-benzoquinone (Q) and *p*-chloranil (ClQ) compounds were isolated as dark brown, microcrystalline solids. The other four

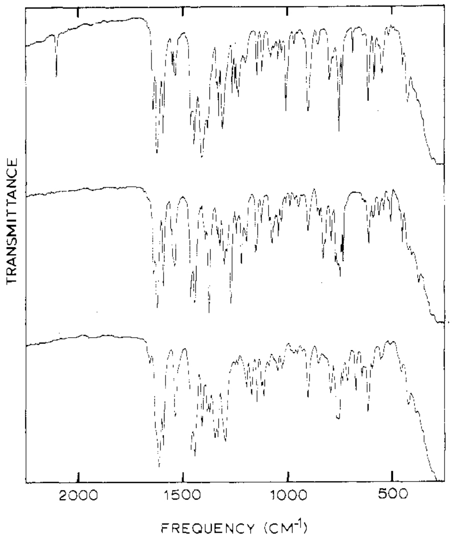


Figure 1. The Nujol mull infrared spectra of $[Fe(salen)]_2(DDQ)\cdot THF$ (top), $[Fe(salen)]_2(NQ)\cdot THF$ (middle), and $[Fe(salen)]_2B\cdot THF$ (bottom).

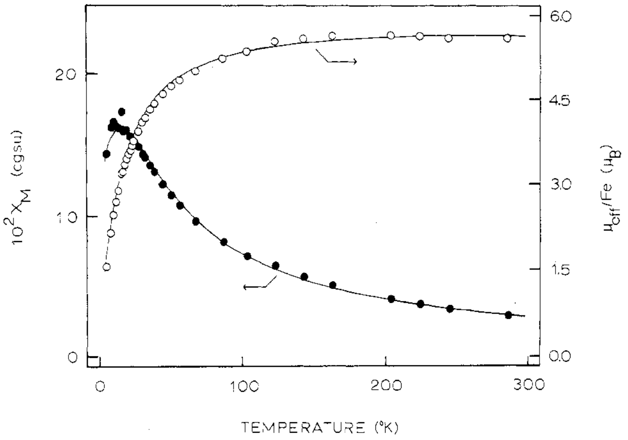


Figure 2. Corrected molar paramagnetic susceptibility (χ_M in cgs units per mole of binuclear complex) and effective magnetic moment per mole of Fe(III) ion (μ_{eff}/Fe) vs. temperature curves for $[Fe(salen)]_2(ClQ)$. The solid lines result from least-squares fitting of the data to theoretical equations; see text.

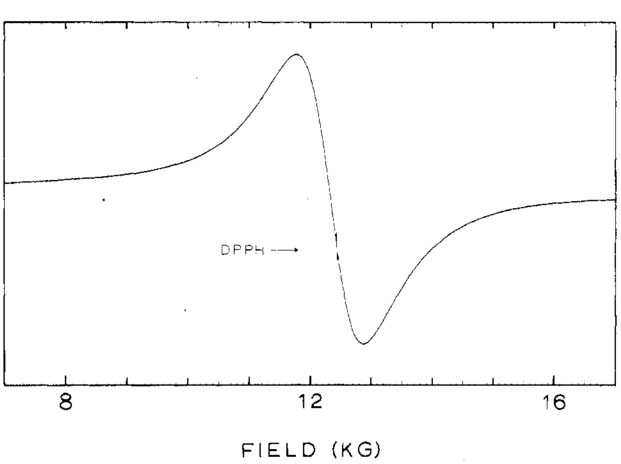


Figure 3. Room-temperature Q-band EPR spectrum of a solid sample of $[Fe(salen)]_2(NQ)\cdot THF$.

compounds prepared in this study were isolated as THF solvates. Previously,[16] the duroquinone compound $[Fe(salen)]_2(DuQ)\cdot THF$ was not indicated to be a THF solvate. However, in this study, analytical data reproducibly pointed to the best formulation as a THF adduct. THF exhibits a strong IR band at ca. 1060 cm^{-1} associated with the C–O stretch absorption, but the complexity of the IR spectra of these complexes precluded a determination of whether THF is present based on the presence of this band. It is important to note that only *one* THF molecule is indicated for these compounds. Thus, there are not two molecules of THF, one for each iron ion. The instance of noncoordinating solvates for these molecules has been noted. For example, crystallographic data for $[Fe(salen)]_2O\cdot 2py$ confirms the presence of an μ-oxo ferric dimer where the pyridine molecules are *not* coordinated to the Fe(III) ion.[23]

No appreciable decomposition in air was observed for $[Fe(salen)]_2(DDQ)\cdot THF$ and $[Fe(salen)]_2Q$ over a 6-month period, as determined by elemental analysis and infrared data. The duroquinone compound has been indicated to decompose after a period of time in the air.[16]

All complexes are relatively insoluble in common organic solvents. Ironically, bianthrone (B), the least soluble of the quinones studied, forms a complex with the greatest solubility in organic solvents.

Infrared spectra were recorded for all six compounds prepared as Nujol mulls in a nitrogen atmosphere. The IR spectra of the DDQ, NQ, and B complexes are illustrated in Figure 1. Four pertinent features should be noted. First, no C=O stretching bands are observed above 1640 cm^{-1} for all but one of the complexes. Second, the bianthrone (B) complex does exhibit a very weak band at 1668 cm^{-1}, which is undoubtedly due to the presence of some unreacted bianthrone. Third, the DDQ complex shows a sharp medium-intensity band at 2208 cm^{-1}, which is assignable to the CN stretching band of the coordinated DDQ. The corresponding IR band for uncoordinated DDQ is barely observable. Fourth, a weak band at ca. 850 cm^{-1} is seen for all of the complexes. The presence of this band could indicate that there is a small amount of oxo-bridged ferric dimer in the samples. Particular care was paid in the synthesis of these compounds under an argon atmosphere to eliminate the formation of such an impurity.

Variable-temperature (4.2–285.5 K) magnetic susceptibility data were obtained for all six compounds; the data are summarized in Tables II–VII.[18] The compounds $[Fe(salen)]_2Q$, $[Fe(salen)]_2(ClQ)$, $[Fe(salen)]_2(DuQ)\cdot THF$, $[Fe(salen)]_2(DDQ)\cdot THF$, $[Fe(salen)]_2(NQ)\cdot THF$, and $[Fe(salen)]_2B\cdot THF$ have effective magnetic moments of 5.38, 5.61, 5.30, 5.22, 5.13, and, 5.72 μ_B, respectively, at 285.5 K. As the sample temperatures are lowered, these μ_{eff} values decrease to 1.68, 1.54, 0.92, 0.84, 0.93 and 4.55 μ_B, respectively, at 4.2 K. The data for $[Fe(salen)]_2(ClQ)$ are illustrated in Figure 2, where it can be seen that μ_{eff} is relatively constant from 285.5 K down to ca. 150 K, whereupon a gradual decrease in μ_{eff} occurs down to ca. 50 K, followed by a more pronounced decrease in μ_{eff} below ca. 50 K. It can also be seen that the corrected molar paramagnetic susceptibility, χ_M, exhibits a maximum at ca. 10 K. Basically the same type of μ_{eff} and χ_M vs. temperature curves are also found for the other *p*-benzoquinone (Q, DuQ, and DDQ) and NQ compounds. The larger quinone (B) compound does not show a maximum in the χ_M vs. temperature curve and the μ_{eff} at 4.2 K is clearly not as reduced in value as found for the other compounds.

The room-temperature Q-band EPR spectrum of $[Fe(salen)]_2(NQ)\cdot THF$ is shown in Figure 3. A single, very broad, isotropic derivative centered at $g = 2.02$ with a line width in excess of 5000 G is observed. This spectrum is reproducible with different sample preparations. Cooling the sample to liquid-nitrogen temperatures has little effect on the signal. However, at liquid-helium temperatures (ca. 6 K) the signal sharpens appreciably to a line width of 1500 G. The compound $[Fe(salen)]_2(DDQ)\cdot THF$ exhibits a similar broad EPR signal at $g = 2.08$, and a broad band barely discernible

Table VIII. Iron-57 Mössbauer Parameters

compound	δ,^{a,b} mm/s 295 K	100 K	4.2 K	ΔE_Q,^{b} mm/s 295 K	100 K	4.2 K
$[Fe(salen)]_2Q$	0.359 (4)	0.448 (2)	0.473 (1)	0.746 (4)	0.792 (2)	0.804 (1)
$[Fe(salen)]_2ClQ$		0.481 (2)	0.486 (1)		1.091 (2)	1.047 (1)
$[Fe(salen)]_2DuQ·THF$		0.497 (1)			0.801 (2)	
$[Fe(salen)]_2DDQ·THF$		0.548 (1)			1.242 (1)	
$[Fe(salen)]_2NQ·THF$		0.524 (2)			0.753 (2)	
$[Fe(salen)]_2B·THF$	0.36 (3)	0.467 (5)	0.493 (2)	0.85 (3)	0.906 (5)	0.897 (2)

	$\Gamma^{b,c}$ 295 K	100 K	4.2 K
$[Fe(salen)]_2Q$	0.208 (3), 0.300 (5)	0.204 (1), 0.287 (2)	0.157 (2), 0.162 (2)
$[Fe(salen)]_2ClQ$		0.244 (1), 0.386 (2)	0.173 (1), 0.169 (1)
$[Fe(salen)]_2DuQ·THF$		0.202 (1), 0.252 (1)	
$[Fe(salen)]_2DDQ·THF$		0.161 (1), 0.161 (1)	
$[Fe(salen)]_2NQ·THF$		0.171 (2), 0.178 (2)	
$[Fe(salen)]_2B·THF$	0.23 (3), 0.24 (3)	0.262 (4), 0.327 (5)	0.276 (3), 0.265 (3)

[a] Relative to Fe metal. [b] Error in last significant figure in parentheses. [c] Half-width at half-maximum listed in the order of increasing velocity of the peak.

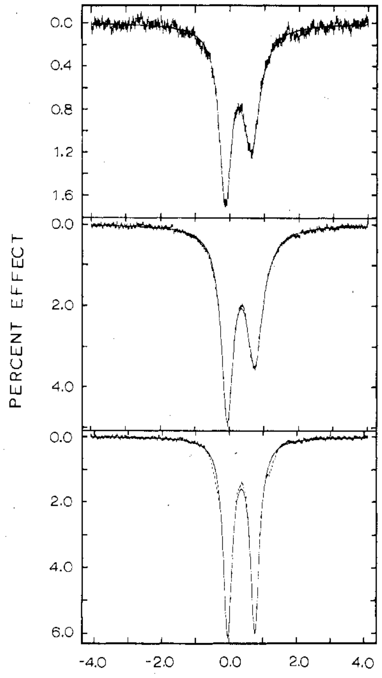


Figure 4. ^{57}Fe Mössbauer spectra of $[Fe(salen)]_2Q$, where Q is the dianion of 1,4-benzohydroquinone, at 295 K (top), 100 K (middle), and 4.2 K (bottom).

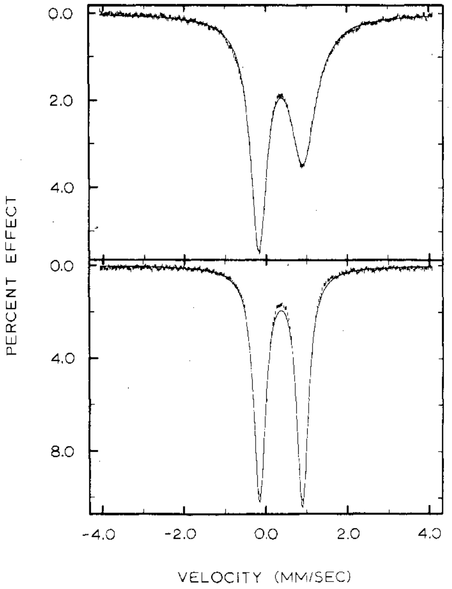


Figure 5. ^{57}Fe Mössbauer spectra of $[Fe(salen)]_2ClQ$, where ClQ is the dianion of 2,3,5,6-tetrachloro-1,4-benzohydroquinone, at 100 K (top) and 4.2 K (bottom).

at $g = 3.77$. On the other hand, no EPR signals were observed for $[Fe(salen)]_2Q$, $[Fe(salen)]_2B·THF$, $[Fe(salen)]_2(ClQ)$, and $[Fe(salen)]_2(DuQ)·THF$ down to liquid-nitrogen temperatures.

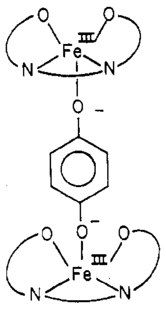
Iron-57 Mössbauer spectra were obtained for all six compounds. The spectra of $[Fe(salen)]_2Q$ at 295, 100, and 4.2 K are shown in Figure 4. As can be seen, the room-temperature spectrum consists of an asymmetric quadrupole-split doublet. Despite the asymmetry, the room-temperature spectrum can be least-squares fit to two Lorentzian line shapes where the areas of the two bands are held equal. This fitting is illustrated in Figure 4 as a solid line, which can be seen to fit very well to the experimental data. As the temperature of the $[Fe(salen)]_2Q$ sample is decreased to 100 K, the asymmetry in the doublet was maintained. The isomer shift and quadrupole splitting for this doublet increased by 0.09 and 0.05 mm/s, respectively, in going from room temperature to 100 K. Further cooling of the same sample to liquid-helium temperature leads to the appearance of a symmetric doublet where the line widths and areas of the two components are essentially equal. There is evidence in the 4.2 K spectrum for a small amount of μ-oxo ferric dimer as an impurity. It is believed that this small amount of impurity was introduced into this sample during the Mössbauer data collection. On cooling of the sample from 100 to 4.2 K, the isomer shift and quadrupole splitting parameters increased by an additional 0.02 and 0.01 mm/s, respectively.

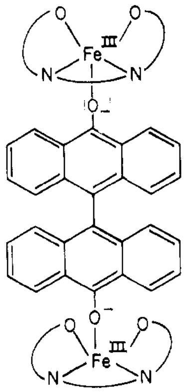
Figure 5 shows the 100 and 4.2 K ^{57}Fe Mössbauer spectra for $[Fe(salen)]_2ClQ$. As can be seen in the figure and as is summarized in Table VIII, the relatively asymmetric appearance of the doublet at 100 K changes when the sample is cooled to 4.2 K. It is also to be noted that the 4.2 K doublet is quite clean in appearance with no evidence of an impurity.

Similar asymmetric quadrupole-split doublets and temperature dependencies were seen for $[Fe(salen)]_2(ClQ)$ and $[Fe(salen)]_2B·THF$ as noted for $[Fe(salen)]_2Q$. The compound $[Fe(salen)]_2(DuQ)·THF$ also exhibits an asymmetric doublet at 100 K. In contrast, however, $[Fe(salen)]_2(DDQ)·THF$ and $[Fe(salen)]_2(NQ)·THF$ give relatively symmetric doublets at 100 K; see Figure 5. The least-squares fitting parameters for the data collected on all six compounds are summarized in Table VIII.

Discussion

The reaction of a *p*-quinone with 2 mol of Fe(salen) gives a binuclear complex comprised of two high-spin (salen)Fe^{III} moieties bridged by the dianion of the corresponding hydroquinone. Thus, the *p*-quinone undergoes a two-electron reduction upon coordination to two (salen)Fe^{II} moieties. The structures of the compounds formed from *p*-benzoquinone and bianthrone are indicated as follows:





It is very likely that the Fe(III) ion coordination geometries are square pyramidal, even for the compounds isolated as THF adducts. Support for the above suggestion of molecular and electronic structure can be drawn from the IR, magnetic susceptibility, and ^{57}Fe Mössbauer data for these compounds.

Considerable IR data are available for quinones in the literature. For example, complete normal-coordinate analyses have been carried out for 1,4-benzoquinone[24] and 1,4-naphthoquinone.[25] Yates et al.[26] studied a series of 22 1,4-benzoquinones and noted a decrease in the carbonyl-stretching frequency upon substitution with electron-donating groups. However, the total range of shifts of ν(C=O) for 1,4-benzoquinones (30–48 cm^{-1} depending on solvent) was not found to be very large. A value of 1664 cm^{-1} has been reported[27] for 1,4-benzoquinone. An examination of the IR spectra for the six compounds prepared in this study shows that there is no band seen at ca. 1660 cm^{-1}. An IR band is seen at ca. 1620 cm^{-1} for all of the compounds; however, comparison with the IR spectra of Fe(salen) and $[Fe(salen)]_2O$ shows that this band is assignable to the ligand $(salen)^{2-}$. In fact, the large number of IR bands seen for Fe(salen) makes it very difficult to identify the carbonyl-stretching frequency for the six compounds. It appears that the best that can be said is that the ν(C=O) band has undergone an appreciable shift to lower frequencies. This is a clear indication that the *p*-quinone has undergone a reduction to either a semiquinone or a hydroquinone.

The ^{57}Fe Mössbauer data summarized in Table VIII clearly indicate that in each of the six compounds there is only one type (relatively narrow line widths) of iron site and that it is most likely a high-spin Fe(III) ion. Relative to iron metal, the range of isomer shifts for high-spin, $S = {}^5/_2$ Fe(III) complexes is ca. +0.25 to +0.60 mm/s,[28] a range that encompasses the values given in Table VIII. For comparison, it is noted that the range of isomer shifts for high-spin, $S = 2$ Fe(II) complexes is ca. +0.8 to +1.5 mm/s relative to iron metal. For example, the isomer shift range was found in a very recent study[29] to be 0.85–0.91 mm/s for a series of high-spin, square-pyramidal, Fe(II) complexes of a macrocyclic ligand. The quadrupole splittings (0.8–1.2 mm/s) given in Table VIII are also in keeping with the suggested coordination geometry. The compound $[Fe(salen)]_2O$ gives a spectrum at 77 K that is characterized by $\delta = 0.46$ mm/s (Fe) and $\Delta E_Q = 0.78$ mm/s,[30] parameters that are very similar to those observed in this study for $[Fe(salen)]_2Q$, $[Fe(salen)]_2(DuQ)\cdot THF$, and $[Fe(salen)]_2B\cdot THF$. The quadrupole splittings observed for $[Fe(salen)]_2(ClQ)$ and $[Fe(salen)]_2(DDQ)\cdot THF$, 1.091 and 1.242 mm/s at 100 K, respectively, are larger and could signal a somewhat greater distortion from idealized square-pyramidal coordination geometry. The two quinone moieties in these compounds do possess sterically large ortho substituents.

The 285.5 K μ_{eff} values found for the six compounds in this study range from 5.1 to 5.7 μ_B and further substantiate the presence of high-spin Fe(III) ions. In a recent study[29] of a series of high-spin, square-pyramidal Fe(II) complexes, μ_{eff} values ranging from ca. 5.1 to 5.3 μ_B at 270 K were observed. This range does overlap somewhat with the range observed for the present six compounds, but when all facts are considered, it is clear that the present complexes contain two high-spin Fe(III) ions.

Figure 2 shows that μ_{eff} for $[Fe(salen)]_2(ClQ)$ does decrease with decreasing temperature. This behavior is found for all six compounds and is a reflection of an *intra*molecular antiferromagnetic exchange interaction between the two $S = {}^5/_2$ ions in each of the six binuclear compounds. Such an exchange interaction between two $S = {}^5/_2$ ions can be largely accounted for with an isotropic exchange spin Hamiltonian of the form $\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$ where $\hat{S}_i$ is the spin operator on each of the two metal centers and J is the exchange parameter, which is a gauge of the magnitude of the interaction. An exchange-coupled, $S_1 = S_2 = {}^5/_2$ complex has electronic states with a total spin of $S' = 5, 4, 3, 2, 1$, and 0. It is the characteristic of such an interacting ferric dimer that even for a weak interaction the variation in Boltzmann distribution over the S' states as a function of temperature is gradual and has an effect even at high temperatures. Thus, even a weak antiferromagnetic exchange interaction can influence the μ_{eff} values at 285.5 K and this could partially explain why the observed values are below the spin-only value of 5.9 μ_B.

The theoretical equation for the corrected molar paramagnetic susceptibility (χ_M) of an $S_1 = S_2 = {}^5/_2$ exchange-coupled dimer incorporating an axial single-ion zero-field interaction has been reported.[31] The spin Hamiltonian is

$$\hat{H} = g\beta\hat{H}_z\cdot\hat{S}_z + g\beta(\hat{H}_x\cdot\hat{S}_x + \hat{H}_y\cdot\hat{S}_y) + D[\hat{S}_z^{\,2} - {}^1/_3S(S+1)] - 2J\hat{S}_1\cdot\hat{S}_2$$

The Hamiltonian matrices are numerically diagonalized as a function of magnetic field to obtain the paramagnetic susceptibility of the dimer. A least-squares fitting computer program was used to fit the data for the six compounds in this study to the reported equations.[31] For each compound, there are three parameters: J the exchange parameter, g the average electronic g factor (it was assumed that $g_{\parallel} = g_{\perp}$), and D the single-ion zero-field splitting parameter. In general the approach used for each compound was to fit the high-temperature data to a g value (with J and D set to zero) and then the g value so obtained was held constant as J and D were varied to fit the data set.

The variable-temperature magnetic susceptibility data of $[Fe(salen)]_2(ClQ)$ were fit to the theoretical equations to give $J = -2.0$ cm^{-1}, $g = 1.98$, and $D = +0.000\,267$ cm^{-1}. The theoretical fits to both the μ_{eff} and χ_M vs. temperature curves are indicated in Figure 2 as solid lines. It can be seen that the fit is reasonable, which verifies the suggestion that there is an antiferromagnetic exchange interaction present in a binuclear complex. The single-ion zero-field splitting parameter is quite small. It was found that incorporating this parameter into the fitting approach had little effect upon the value of J obtained.

The magnetism data for the other five compounds were analyzed in the same manner and Table IX summarizes the parameters obtained for these compounds. As can be seen,

Table IX. Parameters Resultant from Least-Squares Fitting the Susceptibility Data

compound	J, cm^{-1}	10^4D, cm^{-1}	g_{av}
$[Fe(salen)]_2Q$	−2.5	5.8	1.95
$[Fe(salen)]_2ClQ$	−2.0	2.7	1.98
$[Fe(salen)]_2DDQ\cdot THF$	−5.8	1.7	1.95
$[Fe(salen)]_2DuQ\cdot THF$	−4.0	1.2	1.90
$[Fe(salen)]_2NQ\cdot THF$	−4.9	3.1	1.90
$[Fe(salen)]_2B\cdot THF$	−0.21	2.0	1.98

the four dianionic hydroquinones resulting from the 1,4-benzoquinones support an antiferromagnetic interaction where J varies from -2.0 to -5.8 cm^{-1}. There does *not* seem to be any simple relationship between the magnitude of the interaction and the electron-withdrawing or -donating properties of the substituents. The only naphthohydroquinone-bridged system has a J value of -4.9 cm^{-1}. As expected, the dianionic hydroquinone of bianthrone bridging between two (salen)Fe^{III} moieties leads to the weakest interaction with $J = -0.21$ cm^{-1}. The fact that this last molecule does show a weaker interaction establishes that the interactions in the other compounds result from exchange interactions, not zero-field interactions. It is interesting to compare the magnitude of the antiferromagnetic exchange interactions observed in these hydroquinone-bridged Fe(III) dimers with previous results. There have been several studies of μ-oxo-bridged Fe(III) dimers and for nonheme complexes the exchange parameters have been found[32] to fall in the range of -90 to -100 cm^{-1}. The di-μ-hydroxo bridging found[33] for $[Fe(pic)_2OH]_2$, where pic$^-$ is the anion of picolinic acid, supports a weaker interaction with $J = -8$ cm^{-1}. The magnitude of this latter interaction is very close to those found for the hydroquinone-dianion-bridged Fe(III) dimers. Thus, it is clear that the antiferromagnetic interaction does not depend simply on the Fe–Fe distance, but it is a reflection of the details of the electronic structure of the bridging species.

The quadrupole-split doublet asymmetries and temperature dependencies observed in the ^{57}Fe Mössbauer spectra of several of the compounds (see Figure 4) deserve further comment. Asymmetric quadrupole-split doublets may be explained in several ways. Partial orientation of sample crystallites in the sample container, as observed[34] for $Fe_2(CO)_9$, is one possible explanation. Because symmetric doublets were observed at liquid-helium temperature (see Figures 4 and 5), this explanation is not applicable. Goldanski[35] and Karyagin[36] suggested that anisotropy in the recoil of the ^{57}Fe center should produce asymmetry in the $^3/_2 \leftarrow {}^1/_2$ doublet, if a site distortion from octahedral symmetry is present. The Goldanski–Karyagin effect leads to a change of relative peak areas of the two components of a doublet as a function of temperature. With a change in temperature, the line widths of the component lines of a doublet remain unchanged while the areas change. The asymmetry is decreased at low temperature. This second explanation also does *not* appear to be applicable, because we have observed for our compounds that the best fit of spectral data is obtained when the areas of the high and low velocity peaks of one doublet are set equal.

Asymmetry in a quadrupole-split doublet and broadening of lines in a Mössbauer spectrum may be attributed to paramagnetic relaxation of the Fe(III) ion. It has been shown[37] that such asymmetry is possible when the spin-relaxation rate is comparable to the Larmor precession frequency of the nucleus as it is subjected to the internal hyperfine field generated by the unpaired electron spins. For an exchange-interacting Fe(III) dimer at 4.2 K, most of the molecules are in the diamagnetic $S' = 0$ state; there is no hyperfine field and the doublet is symmetric. At higher temperatures, other dimer states where $S' \neq 0$ become populated and slow relaxation of the spins leads to a magnetic hyperfine broadening and an asymmetric doublet. This is why $[Fe(salen)Cl]_2$ ($J = -7.5$ cm^{-1})[38] gives a symmetric spectrum[39] for temperatures less than ca. 6 K, whereas the $[Fe(salen)]_2O$ ($J = -95$ cm^{-1})[40] spectrum[41] is symmetric for $T = 80$ K. Buckley et al.[42] have shown that the interactions in these types of molecules are *inter*molecular in nature. It is clear that the asymmetric doublets and temperature dependence of asymmetry that we see for our complexes is most likely due to this *inter*molecular spin–spin relaxation. In this regard, it is important to note that $[Fe(salen)]_2(DDQ)\cdot THF$ and $[Fe(salen)]_2(NQ)\cdot THF$ exhibit symmetric quadrupole-split doublets at liquid-nitrogen temperature (see Figure 5) and it is only these two compounds that show EPR signals.

The p-quinones studied in this work can only oxidize the iron ions to Fe(III). It would be interesting to react (salen)Fe^{II} with a p-benzoquinone that has bulky substituents at the 2 and 6 positions such that only a 1:1 complex would form. This could result in an Fe(III) complex with a semiquinone ligand; the properties of this type of complex would be interesting.

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Registry No. $[Fe(salen)_2]_2Q$, 41180-62-5; $[Fe(salen)]_2ClQ$, 41119-37-3; $[Fe(salen)]_2DuQ$, 41119-36-2; $[Fe(salen)]_2DDQ$, 67163-17-1; $[Fe(salen)]_2NQ$, 67163-18-2; $[Fe(salen)]_2B$, 67163-19-3.

Supplementary Material Available: Tables I (analytical data) and II–VII (experimental and calculated magnetic susceptibility data for the six compounds studied) (7 pages). Ordering information is given on any current masthead page.

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Magnetic Exchange Interactions in Binuclear Transition-Metal Complexes. 17. Benzidine and *p*-Phenylenediamine, Extended Aromatic Diamine Bridging Ligands in Binuclear Copper(II) 2,2′,2″-Triaminotriethylamine and Vanadyl Bis(hexafluoroacetylacetonate) Complexes[1]

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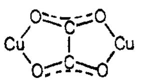
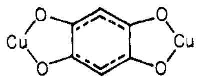
The preparation and magnetic properties are reported for a series of ten binuclear copper(II) complexes of the form $[Cu_2(tren)_2(DA)](Y)_4$, where tren is 2,2′,2″-triaminotriethylamine, DA represents an aromatic diamine such as *p*-phenylenediamine (PPD), durenediamine (DDA), benzidine (BZD), *o*-tolidine (OT), or 4,4′-methylenedianiline (MDA) and Y^- is variously NO_3^-, ClO_4^-, or PF_6^-. Additionally, three vanadyl complexes of the form $[VO(hfac)_2]_2(DA)$ have been prepared, where $hfac^-$ is 1,1,1,5,5,5-hexafluoroacetylacetonate and DA is PPD, DDA, or BZD. The copper(II) binuclear complexes are the first discrete compounds to be isolated containing redox-active aromatic diamines. Variable-temperature (4.2–286 K) magnetic susceptibility and EPR data are reported for all complexes. Antiferromagnetic exchange interactions are found for all copper(II) complexes with exchange parameters which range from ca. $-3\ cm^{-1}$ for the BZD-bridged complexes to nearly $-35\ cm^{-1}$ for the PPD-bridged complexes. No interactions could be detected in the vanadyl complexes with PPD and DDA, but $[VO(hfac)_2]_2(BZD)$ was found to contain only one unpaired electron per binuclear complex. A molecular orbital analysis of the aromatic diamines reveals a tendency to favor a predominantly σ superexchange pathway between the two distorted trigonal-bipyramidal copper(II) centers, although a distinct separation of σ and π orbitals can not be found. These results in conjunction with the recently determined structure of $[Cu_2(tren)_2(BZD)](NO_3)_4$ demonstrate that electrons can exchange between two copper(II) ions separated by more than 12 Å via the BZD bridging group. The interrelationships between the interactions involved in binuclear exchange-interacting metal complexes and inner-sphere electron transfer between two metal complexes are presented.

Introduction

The previous papers[1,3–16,18] in this series have sought to establish various criteria for judging the viability of a particular single-atom or polyatomic bridging unit to support a magnetic exchange interaction between two paramagnetic metal ions. Much of this work has been concerned with exchange interactions in binuclear or dimeric copper(II) complexes and has indicated that the strength of the exchange interaction depends primarily upon the symmetry and energy of the copper(II) ion ground state relative to the highest occupied molecular orbitals of the bridging moiety. For example, in binuclear copper(II) complexes bridged by oxalate,[12] squarate,[12] and the dianions of 2,5-dihydroxybenzoquinones,[13] as shown below, the largest exchange interaction is found for the





μ-oxalate complex as expected on the basis of the Cu–Cu separation, but the next largest interaction is found for the dihydroxybenzoquinone complex and not the squarate complex. Apparently, the greater number of proper symmetry orbitals and their energy proximity to the copper(II) orbitals in the dihydroxybenzoquinone dianion accounts for the greater interaction as compared to the squarate orbitals. The same trend is observed for nickel(II) complexes bridged by these dianions.

Recently, our work[11–14,17,18] has emphasized the importance of the transition-metal ground state in propagating an exchange interaction across a polyatomic bridging unit. In particular, trigonal-bipyramidal complexes of copper(II) with 2,2′,2″-triaminotriethylamine (tren) have been found to be quite effective in obtaining an exchange interaction across an extended bridging moiety. Initially, "outer-sphere" dimers of the form $[Cu_2(tren)_2(X)_2](BPh_4)_2$, where X^- is Br^-,[9] Cl^-,[9] OH^-,[9] CN^-,[19] NCO^-,[5] and NCS^-,[5] were prepared and found to show antiferromagnetic interactions with J (in the Hamiltonian $-2J\hat{S}_1\cdot\hat{S}_2$) ranging from -3.5 to $-0.05\ cm^{-1}$. The X-ray crystal structures[9,19] of four of these dimers revealed a novel Cu–X···H–N–Cu hydrogen-bonded pathway for the exchange interactions. Inner-sphere bridged complexes involving the $Cu(tren)^{2+}$ unit have led to larger antiferromagnetic exchange interactions. For example, cyanide[11] and imidazolate[18] bridges have shown exchange interactions of -88 and $-38\ cm^{-1}$, respectively. In an effort to extend the length of the bridging unit and still maintain an exchange interaction between the copper(II) ions, we chose to investigate various aromatic diamines.

Although heterocyclic diamines (i.e., pyrazine and related bifunctional bridges) have been used extensively to study electron dynamical phenomena such as exchange interactions,[20–22] mixed-valence systems,[23–25] and redox reactions,[24,26,27] aromatic diamines as potential mediators of electron exchange

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