Valence Localization in Iron Complexes with *o*-Quinone-Derived Ligands Studied by High Magnetic Field Mössbauer Spectroscopy

Michelle J. Cohn,[1] Chuan-Liang Xie,[2] Jean-Pierre M. Tuchagues,[3a] Cortlandt G. Pierpont,[3b] and David N. Hendrickson*,[3c]

Department of Chemistry—0506, University of California at San Diego,
La Jolla, California 92093-0506, Laboratoire de Chimie de Coordination du CNRS,
Université Paul Sabatier, 31400 Toulouse, France, and Department of Chemistry,
University of Colorado, Boulder, Colorado 80309

Received January 17, 1992

High magnetic field Mössbauer spectroscopy at liquid-helium temperatures is used to characterize the unpaired electrons in five iron complexes with *o*-quinone-derived ligands. The question addressed is whether the residual unpaired electrons resultant after strong antiferromagnetic exchange interactions between paramagnetic ligands and the iron ion are largely metal based or are delocalized throughout the complex. An internal ^{57}Fe hyperfine field of –495 kG was determined from spectra taken in 60- and 51-kG fields for the $S = {}^5/_2$ complex [Fe(saloph)(catH)], where saloph^{2-} is *N,N'*-phenylenebis(salicylideneaminato) and catH$^-$ is the monoprotonated direduced form (i.e., catecholate) of *o*-benzoquinone. This clearly establishes this saloph complex as a high-spin Fe^{III} complex with diamagnetic ligands. The complex [Fe(salen)(3,5-DBSQ)], where salen^{2-} is *N,N'*-ethylenebis(salicylideneaminato) and 3,5-DBSQ is the semiquinonate form ($S = {}^1/_2$) of 3,5-di-*tert*-butyl-*o*-benzoquinone, has been reported to have an $S = 2$ ground state as the result of an exchange interaction between the one $S = {}^1/_2$ ligand and a high-spin Fe^{III} ion. An internal ^{57}Fe hyperfine field of –455 kG was determined for this complex; this is consistent with four unpaired electrons localized on the Fe^{III} ion. An internal ^{57}Fe hyperfine field of –440 kG was determined for [Fe(phenSQ)(phenCAT)(bpy)]·0.5phenQ, which verifies that this complex has an $S = 2$ ground state resultant from a relatively strong antiferromagnetic exchange interaction between *one* semiquinonate ligand and a high-spin Fe^{III} ion. The ligands in this third complex are 2,2'-bipyridine (bpy) and the semiquinonate (phenSQ$^-$) and catecholate (phenCAT^{2-}) forms of 9,10-phenanthrenequinone (phenQ). The internal ^{57}Fe hyperfine fields of –365 and |310| kG for [Fe(3,5-DBSQ)$_3$] and [Fe(phenSQ)$_3$]·phenQ, respectively, clearly indicate $S = 1$ ground states that result from a relatively strong antiferromagnetic exchange interaction between three $S = {}^1/_2$ semiquinonate ligands and a high-spin Fe^{III} ion. The two unpaired electrons in the $S = 1$ complex Fe(3,5-DBSQ)$_3$ are localized on the Fe^{III} ion. A long-range *inter*molecular antiferromagnetic exchange interaction is present in [Fe(phenSQ)$_3$]·phenQ. This compound shows a six-line magnetic field pattern in its Mössbauer spectrum in the absence of an external magnetic field. The above results indicate that all of the complexes have relatively localized bonding between a high-spin Fe^{III} ion and semiquinonate ligands.

Introduction

The electronic structure of transition metal complexes with noninnocent ligands has been of continuing interest. Redox activity, the characteristic of noninnocent ligands, is found for nitrosyl,[4] 1,2-dithiolene,[5] diimine,[6] quinone,[7] and porphyrin ligands. When complexes of these ligands are oxidized or reduced, it is frequently difficult to determine whether the electron is removed from or added to an orbital which is largely metal or ligand in composition. In complexes where there is appreciable covalency in the ligand–metal interaction, the redox-active molecular orbital is, of course, delocalized. There are significant contributions from both ligand and metal atomic orbitals. Such is the case in 1,2-dithiolene complexes.

Initially, it was concluded that oxidation by one electron of high-spin, five-coordinate iron(III) porphyrin complexes gave iron(IV) complexes;[8] however, it is now accepted that these complexes are iron(III) complexes with porphyrin π-cation ligands.[9] An intramolecular magnetic exchange interaction between the single unpaired electron of the porphyrin π-cation ligand and the five unpaired electrons of the high-spin iron(III) ion is present. In certain porphyrin π-cation complexes, such as Fe(OClO$_3$)$_2$(TPP$^\bullet$), the intramolecular magnetic exchange interaction is ferromagnetic.[10] In others, such as [FeCl(TPP$^\bullet$)]$^+$, there is a strong intramolecular antiferromagnetic exchange interaction between the porphyrin unpaired electron and the unpaired electrons of the high-spin iron(III) ion.[10] An $S = 2$ ground state is found for [FeCl(TPP$^\bullet$)]$^+$. Differences in molecular structures, more specifically out-of-plane distances of the iron ion, lead to these dramatic differences in magnitude of exchange interactions. It is interesting to note that Lang and Groves[11] recently found a ferromagnetic exchange interaction between a porphyrin π-cation radical and an iron(IV) ion when an iron(III) porphyrin was oxidized by two electrons. Mössbauer spectroscopy, both with and without an external field, played a crucial role in all of the above characterizations.

---

(1) Present address: Universal Oil Products, Inc., Chicago, IL.

(2) Present address: Department of Chemistry, The University of Sydney, Sydney, NSW 2006, Australia.

(3) (a) Université Paul Sabatier. (b) University of Colorado. (c) University of California at San Diego.

(4) Schoonover, N. M.; Baker, E. C.; Eisenberg, R. *J. Am. Chem. Soc.* **1979**, *101*, 1880.

(5) McCleverty, J. A. *Prog. Inorg. Chem.* **1968**, *10*, 49.

(6) Konig, K.; Herzog, S. *J. Inorg. Nucl. Chem.* **1970**, *32*, 601.

(7) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45.

(8) (a) Felton, R. H.; Owen, G. S.; Dolphin, D.; Forman, A.; Borg, D. C.; Fajer, J. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 504. (b) Phillippi, M. A.; Goff, H. M. *J. Am. Chem. Soc.* **1979**, *101*, 7691.

(9) (a) Gans, P.; Marchon, J.-C.; Reed, C. A.; Regnard, J.-R. *Nouv. J. Chim.* **1981**, 203. (b) Phillippi, M. A.; Goff, H. M. *J. Am. Chem. Soc.* **1982**, *104*, 6026.

(10) (a) Scholz, W. F.; Reed, C. A.; Lee, Y. J.; Scheidt, W. R.; Lang, G. *J. Am. Chem. Soc.* **1982**, *104*, 6791. (b) Buisson, G.; Deronzier, A.; Duée, E.; Gans, P.; Marchon, J.-C.; Regnard, J.-R. *J. Am. Chem. Soc.* **1982**, *104*, 6793. (c) Gans, P.; Buisson, G.; Duée, E.; Marchon, J.-C.; Erler, B. S.; Scholz, W. F.; Reed, C. A. *J. Am. Chem. Soc.* **1986**, *108*, 1223.

(11) Boso, B.; Lang, G.; McMurray, T. J.; Groves, J. T. *J. Chem. Phys.* **1983**, *79*, 1122.

0020-1669/92/1331-5028$03.00/0

Mössbauer spectroscopy has also been important in characterizing iron complexes which have ligands derived from *o*-quinones.[12-16] Mössbauer spectra taken in zero field indicate that all of these complexes have high-spin iron(III) ions. Fe^{III}(semiquinonate)$_3$ complexes have been determined from magnetic susceptibility measurements to have $S = 1$ ground states which result from a strong intramolecular antiferromagnetic exchange interaction between the three $S = {}^1/_2$ semiquinonate ligands and the five iron(III) d electrons. An $S = 2$ ground state was found for iron(III) complexes with a single semiquinonate ligand, including a complex formulated as [Fe(phenSQ)(phenCAT)(bpy)],[15] where bpy is 2,2′-bipyridine and phenSQ$^-$ and phenCAT^{2-} are the semiquinonate and catecholate forms of 9,10-phenanthrenequinone. Unfortunately, for these even-spin systems the detailed nature of the electronic state cannot be determined by EPR spectroscopy. In the present work, the localization of the unpaired-electron-spin density is examined for five *o*-quinone-based complexes by determining the magnitude and nature of their ^{57}Fe paramagnetic hyperfine interaction in large magnetic fields. For the coupled spin systems ($S = 2$ and $S = 1$) the overall spectral splitting ($\hat H_{eff}$) should proportionately reflect the reduced number of unpaired electrons when compared with those of high-spin ferric ($S = {}^5/_2$) species. Moreover, if these spin-coupled complexes can be properly described as containing high-spin ferric ions and formally reduced ligands (implying that there is no significant covalency between the metal and the ligand), then the unpaired electrons should be basically localized on the iron ion. The magnitude and sign of the internal field ($\hat H_{int}$) will reflect the nature of the orbitals containing the unpaired electrons. We have determined an $\hat H_{int}$ for each complex from the effective field and by assuming isotropic spin coupling between the radical anion ligand and the iron ion. The values of hyperfine field have been related to that expected for high-spin ferric complexes.

Experimental Section

^{57}Fe Mössbauer spectra were collected in vertical transmission geometry using a constant-acceleration spectrometer previously described.[17] The applied field was parallel to the γ-ray direction of all spectra.

Variable-field magnetic susceptibility measurements were carried out using a Series 800 VTS-50 SQUID susceptometer (SHE Corp.). Diamagnetic corrections, estimated from Pascal's constants, were used when calculating the molar paramagnetic susceptibilities.

[Fe(phenSQ)$_3$]·phenQ was prepared using a slightly modified literature procedure.[12] A refluxing benzene solution containing Fe(CO)$_5$ and a 10% molar excess of 9,10-phenanthrenequinone (Aldrich, Gold Label) was irradiated for 4 h. The dark-green microcrystalline product was washed with dry hexanes. All manipulations were done in Schlenkware under argon. Anal. Calcd for $FeC_{56}H_{32}O_8$: Fe, 6.28; C, 75.68; H, 3.63. Found: Fe, 6.15; C, 75.01; H, 3.74.

Samples of three of the other four complexes were available from previous studies.[13,15,16] A sample of the compound [Fe(3,5-DBSQ)$_3$], where 3,5-DBSQ is 3,5-di-*tert*-butyl-1,2-benzosemiquinonate, was prepared as reported previously.[12] All physical measurements were made on polycrystalline samples.

Theoretical Background. For high-spin ferric ions (d^5, $S = {}^5/_2$), a Hamiltonian containing only second-order fine structure terms and an isotropic g tensor has been found to be adequate in most cases. The spin Hamiltonian in eq 1 incorporates these approximations and is parametrized in the usual way.[18,19]

$$\hat H_{5/2} = D[\hat S_z^{\,2} - S(S+1)/3] + E(\hat S_x^{\,2} - \hat S_y^{\,2}) + \beta_e g\hat S\cdot\hat H + \hat S\cdot\mathbf{A}\cdot\hat I - g_n\beta_n\hat I\cdot\hat H + \hat I\cdot\mathbf{P}\cdot\hat I \quad (1)$$

In order to describe the magnetic exchange coupling effects of the semiquinone radical anions interacting with the Fe^{III} ion, terms of the form

$$\hat H_J = \sum_{i=2(3,4)} (g\beta_e\cdot\hat S_i\cdot\hat H - 2J\hat S_1\cdot\hat S_i) \quad (2)$$

need to be added to the $\hat H_{5/2}$ Hamiltonian.[20] The term $-2JS_1\cdot S_i$ is the isotropic magnetic exchange Hamiltonian which gauges the spin–spin interaction of S_1 and S_i. The magnetic exchange parameter, $-J$, has been estimated from previous magnetic studies to be greater than 100 cm^{-1} for all of the coupled complexes.[13-15] It is therefore valid to assume for our studies that the exchange term donimates the entire Hamiltonian $\hat H_{5/2} + \hat H_J$, and since $-2J \gg kT$ for our experiments, we can define an effective Hamiltonian for the ground state of the semiquinonate complexes identical in form to eq 1, where S now represents the coupled spin state ($S = 1$ or $S = 2$).

The Hamiltonian can be further simplified in external magnetic fields greater than ~100 G, since the electronic terms will define the quantization axis, and then using the first two terms of eq 1 we can calculate the expectation value (for each direction) of the electronic spin, $\langle S\rangle$. The Mössbauer spectrum can now be described with the spin Hamiltonian in eq 3.

$$\hat H = \hat I\cdot\mathbf{A}\cdot\langle\hat S\rangle - g_n\beta_n\hat I\cdot\hat H_{ext} + \hat I\cdot\mathbf{P}\hat I \quad (3)$$

In the limit of high magnetic fields, low temperatures, and small zero-field splitting values, the spin expectation value, $\langle S\rangle$, will be close to its saturation value; i.e., it will be nearly equivalent to the value of the most negative M_s eigenstate in at least one principal direction.[21,22]

Often an effective magnetic field is defined as $H_{eff} = H_{ext} + H_{int}$,[17] and from eq 3

$$H_{int} = \frac{-A\langle S\rangle}{g_n\beta_n} \quad (4)$$

When the quadrupolar term is small in comparison with the magnetic field term, the overall spectral splitting can be directly equated with H_{eff}.[23,24] A is typically parametrized into three components: the orbital, dipolar, and Fermi contact terms. Even for distorted high-spin Fe^{III} complexes, the isotropic Fermi contact term will generally dominate[25,26] with a value within ±20% of −220 kG per unit spin as long as there is no significant covalency.

The values of H_{int} determined experimentally are for the ($S = 2$ or $S = 1$) ground state of the semiquinonate complex. With the Wigner–Eckart theorem, we can relate these H_{int} values for the coupled states to the expectation value for the Fe^{III} ion in the complex. The proportionality constant C relating the H_{int} value to the contribution from the Fe^{III} ion is given in eq 5. In this equation $\hat S_{1z}$ is the z component of the spin on

$$C = \frac{\langle SM|\hat S_{1z}|SM\rangle}{\langle SM|\hat S_z|SM\rangle} = \frac{(SM|(\hat S\cdot\hat S_1)|SM'\rangle\delta_{MM'}}{S(S+1)} \quad (5)$$

the Fe^{III} ion and $\hat S_z$ is the z component of the spin of the ground state. For a Fe^{III} complex with one semiquinonate ligand, the ground state has $S = 2$. In this case, the value of $\hat S_1\cdot\hat S$ is obtained from eq 6, where S_2

$$\hat S_1\cdot\hat S = {}^1/_2(\hat S_1^{\,2} + \hat S^2 - \hat S_2^{\,2}) \quad (6)$$

$= {}^1/_2$ is the spin on the single semiquinonate ligand. Thus, for this $S = 2$ complex, $C = {}^7/_6$. The saturation field in the spin 2 coupled system

---

(12) Buchanan, R. M.; Kessel, S. L.; Downs, H.; Pierpont, C. G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1978**, *100*, 7894.

(13) Kessel, S. L.; Emberson, R. M.; Debrunner, P. G.; Hendrickson, D. N. *Inorg. Chem.* **1980**, *19*, 1170.

(14) Lynch, M. W.; Buchanan, R. M.; Pierpont, C. G.; Hendrickson, D. N. *Inorg. Chem.* **1981**, *20*, 1038.

(15) Lynch, M. W.; Valentine, A.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1982**, *104*, 6982.

(16) Tuchagues, J.-P. M.; Hendrickson, D. N. *Inorg. Chem.* **1983**, *22*, 2545.

(17) Cohn, M. J.; Timken, M. D.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1984**, *106*, 6683.

(18) Abragam, A.; Bleaney, B. *Electron Paramagnetic Resonance of Transition Metal Ions*; Clarendon Press: Oxford, U.K., 1970.

(19) Lang, G. *Q. Rev. Biophys.* **1970**, *3*, 1.

(20) Schulz, C. E.; Rutter, R.; Sage, J. T.; Debrunner, P. G.; Hager, L. P. *Biochemistry* **1984**, *23*, 4743.

(21) Lang, G.; Aasa, R.; Garbett, K.; Williams, R. J. P. *J. Chem. Phys.* **1971**, *55*, 4539.

(22) Wickman, H. H.; Wertheim, G. K. *Phys. Rev.* **1966**, *148*, 211.

(23) Knudsen, J. E. *J. Phys. Chem. Solids* **1977**, *38*, 883.

(24) Knudsen, J. E. *J. Phys. Colloq. C6* **1976**, *37*, 735.

(25) Oosterhuis, W. T. *Struct. Bonding* **1974**, *20*, 59.

(26) Münck, E.; Champion, P. M. *J. Phys. Colloq. C6* **1974**, *35*, 33.

(27) Griffith, J. S. *The Theory of Transition Metal Ions*; University Press: Cambridge, U.K., 1964; p 440.

is then expected to be

$$H_{\text{sat}}^{S=2} = \frac{-CA\hat{S}_z}{\beta_n g_n} = \frac{-{}^7/_6 A(2)}{\beta_n g_n} \tag{7}$$

For an isolated Fe^{III} ion it is

$$H_{\text{sat}}^{S_1=5/2} = \frac{-A\hat{S}_{1z}}{\beta_n g_n} = \frac{-{}^5/_2 A}{\beta_n g_n} \tag{8}$$

The ratio of uncoupled to coupled values of H_{int} is ${}^5/_2 \div {}^7/_3 = {}^{15}/_{14}$. For a $S = 2$ complex, the contribution from the Fe^{III} ion is calculated as ${}^{15}/_{14}$th of the coupled H_{int} value.

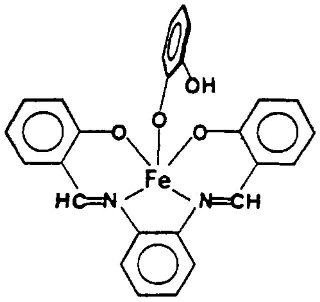
For a Fe^{III} complex with three semiquinonate ligands, the ground state has $S = 1$. By use of the Kambe coupling approach[28] with $\hat{S}_A = \hat{S}_2 + \hat{S}_3 + \hat{S}_4$ for the three semiquinonates, it can be found that

$$\hat{S}_1 \cdot \hat{S} = {}^1/_2(\hat{S}_1{}^2 + \hat{S}^2 - \hat{S}_A{}^2) \tag{9}$$

The $S = 1$ ground state is found when $S_A = {}^3/_2$, which gives for the proportionality constant $C = {}^7/_4$. In this case, the ratio of uncoupled to coupled values of H_{int} is ${}^5/_2 \div {}^7/_4 = {}^{10}/_7$.

Results and Discussion

An $S = {}^5/_2$ Ground-State Complex. A schematic drawing of the molecular structure of the compound [Fe(saloph)(catH)] (**1**), where $saloph^{2-}$ is *N,N'*-phenylenebis(salicylideneaminato) and $catH^-$ is the monoprotonated direduced form of *o*-benzoquinone (i.e., monoprotonated catecholate), is shown as follows:



This was selected as a good model for a high-spin ferric, $S = {}^5/_2$ complex on the basis of previous structural, magnetic, and spectroscopic characterizations. [Fe(saloph)(catH)] has been shown to crystallize[30] with a square-pyramidal geometry about the iron ion where the monoprotonated catecholate ligand is coordinated in a monodentate fashion in the axial coordination site. Magnetic susceptibility measurements[31] showed a magnetic moment of 5.92 ± 0.3 μ_B over the entire temperature range of 4.2–300 K; this is consistent with a high-spin ferric ion with *small* zero-field splitting. There was, however, a small positive Curie–Weiss constant of 1.1 ± 0.1 K noted. A Mössbauer spectrum[16] taken in zero magnetic field at 11 K showed $\Delta E_Q = 0.539$ mm/s and isomer shift of $\delta = 0.462$ mm/s, which are typical of a high-spin Fe^{III} ion.

The Mössbauer spectrum for compound **1** shown in Figure 1A was taken in a 60-kG applied magnetic field. An internal ^{57}Fe hyperfine field of −495 kG was determined from the overall spectral splitting and the external field (see Table I). A spectrum taken at a slightly reduced field (51 kG) confirmed that the principal component of the hyperfine interaction is negative. The magnitudes of the hyperfine splitting were determined in this work by simply fitting the spectral features to Lorentzian line shapes. To obtain more accurate evaluations of the hyperfine splittings, the spectra should be simulated as powder spectra. However, fitting the spectrum for compound **1** as a powder average showed us that for the purposes of the present correlation the magnetic fields determined by Lorentzian line shape analysis are sufficiently accurate. The relatively sharp, essentially four-line pattern (peaks 2 and 5 are absent from a six-line magnetic pattern) is consistent with a ground electronic state whose spin expectation value and direction are determined by the parallel external field. A primarily Fermi contact interaction between the five unpaired d electrons and the ^{57}Fe nucleus fits the above experimental observations.

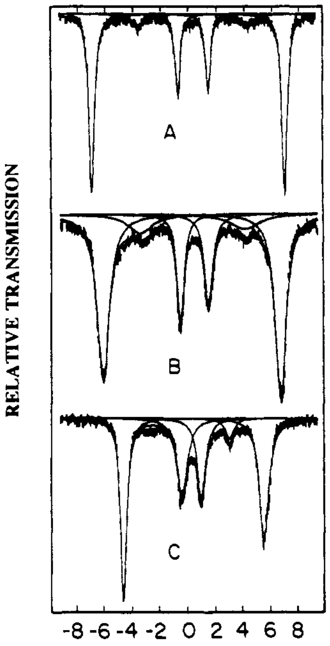


Figure 1. Mössbauer spectra taken in a 60-kG parallel field of polycrystalline samples: (A) [Fe(saloph)(catH)] (**1**), $S = {}^5/_2$, $T = 4.5$ K; (B) [Fe(salen)(3,5-DBSQ)] (**2**), $S = 2$, $T = 4.8$ K; (C) [Fe(3,5-DBSQ)$_3$] (**4**), $S = 1$, $T = 1.8$ K. Spectra were fit with Lorentzian line shape only to determine peak positions.

The average hyperfine field obtained for complex **1** is comparable with values obtained for other well-characterized high-spin ferric complexes of both the five- and the six-coordinate type. For example, the tris(catecholate) complex $(C_5H_{12}N)_3$-$[Fe^{III}(catecholate)_3]\cdot H_2O$[32] has a hyperfine field value of |502| kg,[33] while $[Fe(H_2O)_6{}^{3+}]$[23] shows |580| kG[33] for a FeO_6 octahedral site. The internal field found for some pentacoordinate porphyrin complexes,[34] e.g., (methoxy)Fe^{III}(octaethylporphyrin), range from −490 to −511 kG. Heme-containing proteins such as metmyoglobin hydrate have saturation field values from −450 to −550 kG.[26,35] Iron–sulfur proteins, which have tetrahedral sulfur coordination about the high-spin Fe^{III} sites, have internal field values ranging from −360 to −375 kG and are assumed to have a high degree of covalency.[36,37] It is clear that compound **1** has an internal field value appropriate for a high-spin ferric ($S = {}^5/_2$) state with little covalency (i.e., there is little leakage of the unpaired spin density out onto the ligands).

$S = 2$ Ground-State Complexes. High-field Mössbauer spectra were obtained for the two compounds which have a single semiquinonate ligand. The compound [Fe(salen)(3,5-DBSQ)] (**2**), where salen is *N,N'*-ethylenebis(salicylideneaminato) and $3,5\text{-}DBSQ^-$ is the semiquinonate form of 3,5-di-*tert*-butyl-*o*-benzoquinone, has been previously reported[13] to have an effective magnetic moment of 4.87 μ_B at 286 K and to exhibit little temperature dependence in μ_{eff} essentially down to liquid helium temperature, again indicating negligible zero-field splitting values. This magnetic moment, which is very near the spin-only value for four unpaired electrons, is a clear indication of the presence of an intramolecular antiferromagnetic exchange interaction between the single semiquinonate radical ligand and the five unpaired electrons of the high-spin ferric ion. The nearly

---

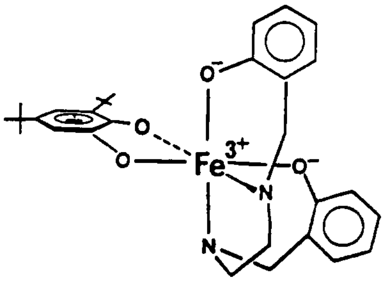
(28) Kambe, K. *J. Phys. Soc. Jpn.* **1950**, *5*, 48.
(29) Mørup, S. *Mössbauer Eff. Methodol.* **1974**, *9*, 127.
(30) Heistand, R. H., II; Roe, A. L.; Que, L., Jr. *Inorg. Chem.* **1982**, *21*, 676.
(31) Heistand, R. H., II; Lauffer, R. B.; Fikrig, E.; Que, L., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 2789.

Table I. ^{57}Fe Hyperfine Values for Iron Complexes with *o*-Quinone-Derived Ligands

compound	T (K)	tot. spin[a]	H_{eff} (kG)[b]	H_{int} (kG)[c]	$H_{5/2}$ (kG)[d]
[Fe(saloph)(catH)] (**1**)	4.5	5/2	−435	−495	
[Fe(salen)(3,5-DBSQ)] (**2**)	4.5	2	−395	−455	−487
[Fe(phenSQ)(phenCAT)(bpy)]·0.5phenQ (**3**)	4.8	2	−380	−440	−471
[Fe(3,5-DBSQ)$_3$] (**4**)	1.8	1	−305	−365	−521
[Fe(phenSQ)$_3$]·phenQ (**5**)	4.5	1	|310|	|310|	−442

[a] Determined by magnetic susceptibility studies. [b] Magnitude obtained from the overall spectral splitting. The sign of the major component of the total field was determined by varying the external field for compounds **1**–**4**. Compound **5** antiferromagnetically orders, so this determination was not possible. [c] Calculated from $H_{\text{eff}} = H_{\text{int}} + H_{\text{ext}}$, where H_{ext} = 60 kG for compounds **1**–**4** and H_{ext} = 0 for compound **5**. [d] Internal field relative to $S = {}^5/_2$. Tabulated for comparison with compound **1**.

temperature-independent behavior of μ_{eff} indicates the exchange interaction is quite strong. The susceptibility data have been least-squares-fitted to an isotropic exchange Hamiltonian of the form $-2JS_1{\cdot}S_2$, where $S_1 = {}^1/_2$ and $S_2 = {}^5/_2$, to give $-J > 600$ cm^{-1}, and therefore the $S = 2$ state is the ground electronic state.[13] A compound with very similar magnetic properties,[13] [Fe(salen)(phenSQ)] (where phenSQ is the semiquinonate form of 9,10-phenanthrenequinone), has recently been structurally characterized.[38] The salen ligand in this compound has been forced to assume a nonplanar, "fold-back" geometry[38–40] to accommodate the chelating semiquinonate ligand. The semiquinonate formulation of the chelating ligand was confirmed by C–O and C–C bond distances. In analogy with these results, the molecular structure of **2** is likely to have a distorted octahedral coordination geometry as indicated in the following diagram:



This is in agreement with earlier suggestions.[13] The zero-field Mössbauer parameters obtained for complex **2** (ΔE_Q = 0.901 mm/s, δ = 0.523 mm/s) are reasonable for a distorted high-spin Fe^{III} ion.

Spectrum B in Figure 1 is the 60-kG-applied-field Mössbauer spectrum of **2**. In comparison to the spectrum for compound **1**, the most noticeable change is the reduction in the overall splitting, while the spectral appearance (i.e., essentially a four-line pattern) is the same. The reduced internal field value (see Table I) is a direct reflection of the smaller spin value for the ground state of this compound. A value of H_{int} = 455 kG is obtained from the spectrum for complex **2**. The values of H_{int} contributed by the Fe^{III} ion in complex **2** is calculated to be ${}^{15}/_{14}$(−455 kG) = −487 kG. This is reasonable for a high-spin Fe^{III} ion in a distorted octahedral N$_2$O$_4$ environment and confirms the hypothesis that essentially no *transfer* of unpaired electron density has taken place from the metal to the ligands; only a magnetic exchange interaction is present.

The other $S = 2$ ground-state compound studied which has a single semiquinonate ligand is the interesting mixed-valence complex [Fe(phenSQ)(phenCAT)(bpy)]·0.5phenQ (**3**), where phenSQ, phenCAT, and phenQ are the semiquinonate, catecholate, and quinone forms of 9,10-phenanthrenequinone, respectively, and bpy is 2,2′-bipyridine.[15] The magnetic moment at 245 K for this compound is 4.90 μ_B,[15] a value that stays nearly temperature-independent down to 4.2 K, where the moment is 5.00 μ_B. The description of this compound as having an Fe^{III} ion ($S = {}^5/_2$) with one $S = {}^1/_2$ semiquinonate ligand which is strongly antiferromagnetically interacting with the Fe^{III} ion gives a ground state ($S = 2$) which is consistent with the susceptibility data. The limiting descriptions (i.e., either all weak or all strong magnetic exchange interactions) of other possible formulations, e.g., [Fe^{II}(semiquinonate)$_2$(nitrogen base)] or [Fe^{III}(semiquinonate)$_2$(nitrogen base radical anion)], are not in agreement with the susceptibility data. Zero-field Mössbauer spectra (ΔE_Q = 1.284 (7) mm/s, IS = 0.577 mm/s at 4.2 K) are also consistent with a high-spin ferric ion formulation.

The 4.8 K, 60-kG Mössbauer spectrum for compound **3** is similar in appearance to spectrum B for compound **2** in Figure 1. As can be seen from Table I, the internal field value for this compound, −440 kG, is very close to the value for compound **2**. The internal field calculated for the component high-spin ferric ion, −471 kG, is also quite reasonable for this N$_2$O$_4$ distorted octahedral environment. Thus, complex **3** is also best described as a complex of a high-spin Fe^{III} $S = {}^5/_2$ ion strongly and antiferromagnetically interacting with a single $S = {}^1/_2$ semiquinonate ligand.

$S = 1$ Ground-State Complexes. Complex **4**, [Fe(3,5-DBSQ)$_3$], has a magnetic moment of 2.95 μ_B[12] at 285 K, which remains relatively unchanged (2.64 μ_B at 4.2 K) throughout the temperature range studied. This is indicative of an $S = 1$ ground state arising from a strong intramolecular antiferromagnetic exchange interaction between three $S = {}^1/_2$ semiquinonate radical ligands and an $S = {}^5/_2$ Fe^{III} ion. The magnetic susceptibility data were fitted[14] to a theoretical expression containing a single exchange parameter characterizing the Fe^{III}–semiquinonate interaction. A lower limit of $-J$ = 190 cm^{-1} was determined for this complex, characteristic of a strong magnetic exchange interaction. Mössbauer data taken in a zero external field gave ΔE_Q = 0.763 mm/s and δ = 0.598 mm/s at 4 K.

Spectrum C in Figure 1, obtained at 1.8 K for complex **4** with a 60-kG external magnetic field, has an even smaller H_{eff} than those of the previous three compounds. This is expected for a complex with an $S = 1$ ground state. Very low temperatures were necessary for this compound, as quite efficient relaxation mechanisms are in effect even at 4.2 K. It is difficult to speculate about the relaxation mechanism leading to this; it seems that the bulky *tert*-butyl groups should serve to magnetically dilute the complexes and *slow* down spin–spin relaxation. It is possible that extended intermolecular interactions are just strong enough to help slow the electronic spin flip in the other compounds studied and the presence of the bulky groups prevents this. The peak line width intensity distribution is still indicative of an electronic state

---

(32) Anderson, B. F.; Buckingham, D. A.; Robertson, G. B.; Webb, J.; Murray, K. S.; Clark, P. E. *Nature* **1976**, *262*, 722.
(33) No sign given by authors.
(34) Dolphin, D. H.; Sams, J. R.; Tsin, T. B.; Wong, K. L. *J. Am. Chem. Soc.* **1978**, *100*, 1711.
(35) Münck, E. In *The Porphyrins*; Dolphin, D.; Ed.; Academic Press: New York, 1979; Vol. IV.
(36) Debrunner, P. G.; Münck, E.; Que, L., Jr.; Schulz, C. E. *Iron-Sulfur Proteins*; Academic Press: New York, 1976; Vol. 3, p 381.
(37) Orme-Johnson, W. H.; Sands, R. H. *Iron-Sulfur Proteins*, Academic Press: New York, 1973; Vol. 2, p 195.
(38) Lauffer, R. B.; Heistand, R. H., II; Que, L., Jr. *Inorg. Chem.* **1983**, *22*, 50.
(39) Calligaris, M.; Manzini, G.; Nardin, G.; Randaccio, L. *J. Chem. Soc., Dalton Trans* **1972**, 543.
(40) Hobday, M. D.; Smith, T. D. *Coord. Chem. Rev.* **1972**, *9*, 311.

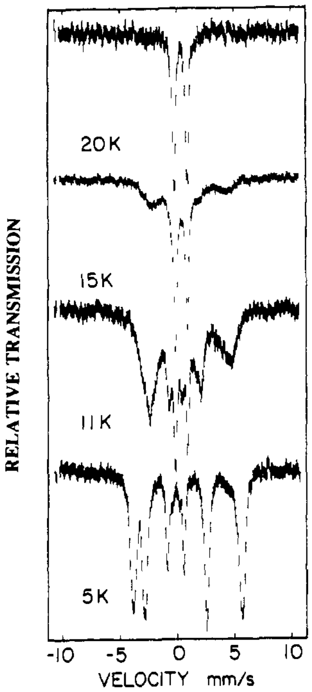


Figure 2. Variable-temperature zero-field Mössbauer spectra of [Fe(phenSQ)$_3$]·phenQ (**5**), which has an $S = 1$ ground state.

which is highly influenced by the external field. This is the expected result for a $S = 1$ ground state whose unpaired electron density resides in the orbitals of a high-spin ferric ion. The magnitude of H_{int}, –365 kG, for the exchange-coupled unit can be related to its component uncoupled spins as previously described. The number calculated for the $S = {}^5/_2$ Fe^{III} ion is –521 kG, a reasonable value for an iron coordinated to six oxygen atoms in a pseudooctahedral geometry.

Complex **5**, [Fe(phenSQ)$_3$]·phenQ, gave a dramatic result in its *zero-field* ^{57}Fe Mössbauer spectrum determined at low temperature (see Figure 2). A magnetic hyperfine pattern is seen at 5 K in *zero* applied field. The Mössbauer spectrum reported previously[12] at 90 K gave the typical high-spin Fe^{III} values of ΔE_Q = 0.924 (4) mm/s and δ = 0.530 (4) mm/s. Theoretically, only slow paramagnetic relaxation or long-range (3-D) intermolecular magnetic ordering[41] can give rise to such a large spectral splitting in zero applied field. Previous magnetic susceptibility measurements[12] (measured in a 13-kG field) showed a fairly sharp maximum in the susceptibility versus temperature plot at ~5 K. The μ_{eff} values showed a marked temperature dependence ranging from 3.43 μ_B at 286 K to 1.52 μ_B at 5 K. The fact that the high-temperature moment is greater than the spin-only value for two unpaired electrons can readily be explained in terms of the magnitude of the exchange interaction. If the antiferromagnetic coupling between the three radical ligands and the high-spin Fe^{III} ion is relatively weak, then the energy separation between the $S = 1$ and $S = 2$ states will be within thermal energy at room temperature, the $S = 2$ excited state will be populated, and the magnetic moment will reflect this population of the $S = 2$ state. The susceptibility data were least-squares-fitted to a theoretical susceptibility expression[14] (assuming isotropic spin coupling) for temperatures above ~200 K to give a value of $-J > 100$ cm^{-1}. The low-temperature data were suggested to be the result *inter*molecular interactions which are antiferromagnetic in origin in order to explain the reduced moment (below spin-only) at temperatures lower than ~60 K. A plot of χ^{-1} versus temperature yielded a straight line between the temperatures of ~10 and 50 K and a Weiss constant of $\Theta \simeq -6$ K, qualitatively indicating the presence of weak antiferromagnetic *inter*molecular interactions. (No broad local maximum was observed in the temperature dependence ($T > T_{\chi(max)}$) of the susceptibility, indicating the presence of low dimensionality;[43,44] the presence of a broad maximum, however, could have been obscured in the temperature dependence of the *intra*molecular exchange interaction.) Since Mössbauer measurements will generally only detect the 3-dimensional ordering of spins,[41,42] the appearance of a sharp six-line pattern gives us an estimate of the Neél temperature. This was seen to occur at ~5 K, in reasonable agreement with the $T_{\chi(max)}$ from susceptibility measurements. The gradual onset of the hyperfine interaction and broadening of the spectra from 15 to ~5 K can be ascribed to relaxation effects, low-dimensional ordering, or a distribution of ordering temperatures.

Mössbauer spectra for complex **5** in applied magnetic fields of 10–60 kG at 5 K showed no change in the overall splitting (average hyperfine field), only an increase in line width as expected for a polycrystalline antiferromagnet in an external field less than that necessary to induce a phase transition.[45] This is in contrast to the behavior expected for a paramagnet whose spin direction will usually be influenced by an external field. In this case, the overall splitting, H_{eff}, will be the vector sum of $H_{int} + H_{ext}$, and for a 60-kG field this change corresponds at most to 2.0 mm/s.

The crystal structure for compound **5** has been reported,[12] and intermolecular interactions were found to be significant. There are two types of close contacts: four-membered "stacks" consisting of two quinone molecules and two ligands and direct overlap of ligands on adjacent molecules. Interplanar separations within the four-membered stack are 3.4–3.5 Å, while the interligand separation is 3.35 Å. It would appear from crystallographic considerations that this compound might have low lattice dimensionality; these sorts of predictions are, of course, often overly simplistic.[46]

It is well-known that the behavior of antiferromagnets in an applied ("disordering") field depend on both the lattice and spin-dimensionality of the system.[43] An attempt was made to learn more about the type of antiferromagnetic interactions present in this compound by observing the magnetization as function of applied field at 4.5 K. The data obtained on a microcrystalline sample from 10 to 49 kG showed no evidence of a phase transition. The magnetization increases monotonically with constant slope to less than 10% of its saturation value. This, unfortunately, does not exclude any of the nine possibilities.[43] The variable-field Mössbauer data are in agreement with these results since no spin-flop or paramagnetic phase transition is observed up to an applied field of 60 kG. For a high-spin Fe^{III} ion, the expected type of spin-dimensionality is described by the Heisenberg model. Many models exist for the behavior of susceptibility with temperature for Heisenberg magnets;[47–49] our situation is complicated by additional parameters necessary for the *intra*molecular exchange interaction.

Regardless of the type of long-range magnetic interaction present, the effective field measured is nearly equivalent to the H_{int} for most high-spin ferric compounds.[50] Even for our spin-coupled cases, we have found that the anisotropy in these compounds is small (as evidenced from small D values leading to four-line Mössbauer patterns). The six-line intensity pattern for this compound is, of course, due to the random orientation

---

(41) Reiff, W. M. In *Chemical Mössbauer Spectroscopy*; Herber, R. H., Ed.; Plenum Press: New York, 1984.

(42) Reiff, W. M. In *Magneto-Structural Correlations in Exchange Coupled Systems*; Willet, R. D., Gatteschi, D., Kahn, O., Eds.; Reidel Publishing Co.: Boston, MA, 1985.

(43) deJongh, L. J.; Miedema, A. R. *Adv. Phys.* **1974**, *23*, 1.

(44) Witteveen, H. T.; Reedijk, J. *J. Solid State Chem.* **1974**, *10*, 151.

(45) Reiff, W. M.; Wong, H.; Frankel, R. B.; Foner, S. *Inorg. Chem.* **1977**, *16*, 1096.

(46) See for example: Carlin, R. L. *Acc. Chem. Res.* **1976**, *9*, 67.

(47) Brown, D. B.; Wrobleski, J. T. *Inorg. Chem.* **1979**, *18*, 498.

(48) McElearney, J. N. *Inorg. Chem.* **1976**, *15*, 823.

(49) O'Connor, C. T. *Prog. Inorg. Chem.* **1982**, *29*, 203.

(50) Chappert, J. *Hyperfine Interact.* **1983**, *13*, 25.

of the effective field and the γ-ray direction and is not a reflection of any spin anisotropy.

The H_{int} value of -442 kG calculated for the Fe^{III} component complex **5** (see Table I) is somewhat lower than the value observed for the other compounds in this study, although it is in a range that has been observed for high-spin ferric compounds.[25] A number of possible explanations exist for the low value. From an experimental consideration, 4.5 K may not be a sufficiently low temperature to completely order the spins (although spectra taken from 5.5 to 4.2 K had nearly the same overall splitting) or the zero-field value, D, for this complex may be large and positive, so that the ground-state wave function is an admixture and the spin-expectation value is consequently smaller. Larger fields would then be required to isolate a "pure" ground electronic state.

The molecular aspects of this compound also seem to offer a plausible explanation for the slightly reduced hyperfine interaction. EPR spectra show superhyperfine structure for uncoupled *o*-semiquinonates[51] which indicate the unpaired electron is delocalized throughout the π-network. It seems very likely that some of the iron unpaired electron density (probably through the same pathway as for the *inter*molecular exchange interaction) has been delocalized onto the ligands; i.e., there is some small covalency in this compound through the π-network of the three highly aromatic ligands. The magnitude of the hyperfine interaction, however, clearly indicates that the overwhelming majority of the unpaired-electron density is still at the iron atom.

Conclusions

The magnetic hyperfine properties of four spin-coupled (*o*-semiquinonato)iron complexes have been presented and compared to those of a closely related high-spin ferric compound. Our basic observation, plotted in Figure 3, is that the number of unpaired electrons found from magnetic susceptibility studies correlates linearly with the hyperfine interaction found at the ^{57}Fe nucleus. This linear correlation, sign of the hyperfine interaction, and isotropic spectral appearance are all indicative of a primarily Fermi contact interaction between these electrons an the ^{57}Fe nucleus, as expected for a high-spin ferric ion. The large magnitude of the hyperfine interaction indicates essentially all of the unpaired-electron density is felt at the iron. This is in agreement with a theoretical study[52] of tris(*o*-quinone)iron complexes which found the unpaired-electron density for Fe(semiquinonate)$_3$ to be in primarily metal-based orbitals.

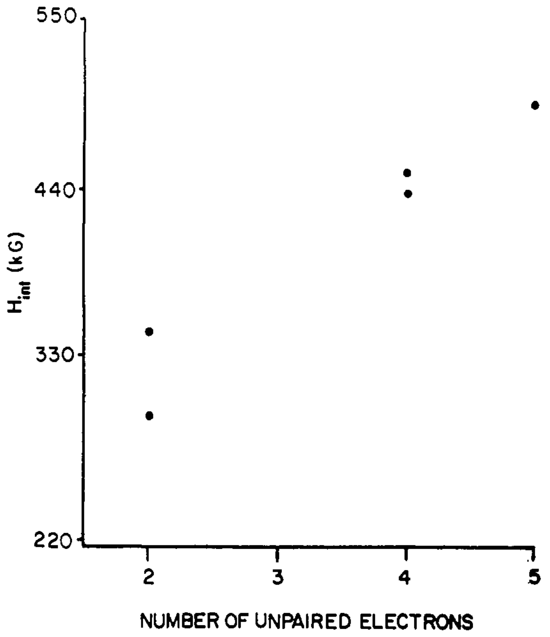


Figure 3. Plot of the correlation between the ^{57}Fe hyperfine field measured by Mössbauer spectroscopy and the number of unpaired electrons determined for each complex by magnetic susceptibility measurements.

By using a vector-coupling approach to find the hyperfine interaction at the component high-spin ferric ion of each exchange-coupled unit, we obtained good agreement of this value with that of the $S = {}^5/_2$ compound of this study and with those of high-spin ferric ions in similar environments in previous studies. There appears to be no significant covalency associated with these complexes, and it is clear that they can be best formulated as having high-spin ferric ions exchange coupled with semiquinonate ligands.

Acknowledgment. We are grateful for support from National Institutes of Health Grants HL 13652 (D.N.H.) and GM 23386 (C.G.P.).

---

(51) Pasimeni, L.; Brustolon, M.; Corvaja, C. *Chem. Phys. Lett.* **1975**, *30*, 249.

(52) Gordon, D. J.; Fenske, R. F. *Inorg. Chem.* **1982**, *21*, 2916.