

# Structural and Magnetic Properties of Tris(*o*-semiquinone) Complexes of Iron(III) and Chromium(III)

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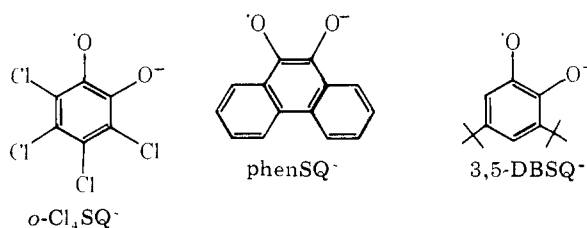
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**Abstract:** The preparation and characterization with physical techniques of tris(*o*-semiquinone) complexes of Fe(III) and Cr(III) are reported. In the case of Fe(III), the complexes are Fe(*o*-Cl<sub>4</sub>SQ)<sub>3</sub>·4Ph, Fe(phenSQ)<sub>3</sub>·phenQ, and Fe(3,5-DBSQ)<sub>3</sub>, where *o*-Cl<sub>4</sub>SQ<sup>-</sup> is tetrachloro-1,2-benzosemiquinone, phenSQ<sup>-</sup> is 9,10-phenanthrenesemiquinone, phenQ is 9,10-phenanthrenequinone, and 3,5-DBSQ<sup>-</sup> is 3,5-di(*tert*-butyl)-1,2-benzosemiquinone. In the case of Cr(III), the complexes are Cr(*o*-Cl<sub>4</sub>SQ)<sub>3</sub>·4Ph and Cr(phenSQ)<sub>3</sub>·anisole. The crystal and molecular structure of Fe(phenSQ)<sub>3</sub>·phenQ has been determined using heavy-atom, least-squares, X-ray methods for 2712 reflections measured on a computer-automated four-circle diffractometer. The dark green complex crystallizes in the triclinic space group *P* $\bar{1}$  with two formula weights in a unit cell with *a* = 8.832 (1) Å, *b* = 15.621 (3) Å, *c* = 16.475 (3) Å,  $\alpha$  = 117.36 (1)°,  $\beta$  = 91.84 (1)°,  $\gamma$  = 91.75 (1)°, *d*(calcd) = 1.465 g cm<sup>-3</sup>, and *d*(exptl) = 1.45 g cm<sup>-3</sup>. The complex consists of weakly interacting Fe(phenSQ)<sub>3</sub> complex molecules and molecules of unreduced quinone. In Fe(phenSQ)<sub>3</sub>, three *o*-semiquinone ligands are chelating the iron ion resulting in a trigonally distorted octahedral coordination geometry. Compared to the dimensions of the solvate phenQ molecule, the dimensions of the ligands in Fe(phenSQ)<sub>3</sub> are substantially changed. The C–C lengths between carbonyl carbon atoms of the ligands average to 1.435 (6) Å, which is 0.1 Å shorter than the length in the phenQ molecule. The average C–O length for the three ligands is 1.283 (3) Å, 0.070 Å longer than the values observed for the quinone. There are appreciable *intermolecular* interactions as result of stacking of phenQ and Fe(phenSQ)<sub>3</sub> molecules. The <sup>57</sup>Fe Mössbauer spectrum for each of the three iron complexes consists of a single quadrupole-split doublet with splitting and isomer shift parameters characteristic of high-spin Fe(III). Variable-temperature (4.2–286 K) magnetic susceptibility data for all five compounds show that in each complex there is an *intramolecular* antiferromagnetic exchange interaction between the unpaired electrons of the three coordinated *S* = 1/2 semiquinone ligands and the unpaired electrons of the high-spin trivalent metal ion. The complex Fe(3,5-DBSQ)<sub>3</sub> behaves as an *S* = 1 complex with two unpaired electrons in the ground state;  $\mu_{\text{eff}}$  is relatively independent of temperature with a value of 2.90 ± 0.05  $\mu_{\text{B}}$ . The other two iron complexes show markedly temperature-dependent  $\mu_{\text{eff}}$  values which is interpreted to mean that the *intramolecular* antiferromagnetic interaction is relatively weak. The two Cr(III) complexes also exhibit temperature-dependent  $\mu_{\text{eff}}$  values with  $\mu_{\text{eff}} \approx 1.1 \mu_{\text{B}}$  at 286 K, dropping to  $\mu_{\text{eff}} \approx 0.35 \mu_{\text{B}}$  at 4.2 K.

## Introduction

Complexes in which a radical ligand is weakly coupled to a paramagnetic transition metal ion through an intramolecular antiferromagnetic interaction exhibit temperature-dependent effective magnetic moments. The temperature dependence arises from thermal population of low-lying excited states. Such complexes are rare; examples include a number of tris(2,2'-bipyridyl radical anion) complexes<sup>4</sup> and a few transition metal complexes with nitroxide ligands.<sup>5</sup>

In this paper, a series<sup>6</sup> of *o*-semiquinone (SQ) complexes of Fe(III) and Cr(III) of general formula M(SQ)<sub>3</sub> are described. Data include magnetic measurements, Mössbauer spectra of the iron complexes, and a single-crystal X-ray structure of the tris(9,10-phenanthrenesemiquinone)iron(III) complex, Fe(phenSQ)<sub>3</sub>·phenQ. The ligands used are as follows.



## Experimental Section

**Compound Synthesis. Cr Complexes.** The preparation of Cr(*o*-Cl<sub>4</sub>SQ)<sub>3</sub> has been described previously.<sup>7</sup> Samples of the related 9,10-phenanthrenesemiquinone and 3,5-di(*tert*-butyl)benzosemiquinone complexes were prepared by a similar procedure using anisole as the solvent medium.<sup>8</sup> The complex Cr(phenSQ)<sub>3</sub> is obtained as an

anisole solvate, Cr(phenSQ)<sub>3</sub>·anisole; the di(*tert*-butyl)semiquinone complex was unsolvated. All three complexes are dark red in color. Satisfactory analytical data were obtained for all complexes.

**Fe Complexes.** Calderazzo has reported the synthesis of Fe(phenSQ)<sub>3</sub> previously.<sup>9</sup> We have found that photolysis of a benzene solution of Fe(CO)<sub>5</sub> and excess 9,10-phenanthrenequinone over the period of 4 h produces the dark green complex which crystallizes from solution with a quinone molecule of crystallization, Fe(phenSQ)<sub>3</sub>·phenQ. The compound Fe(*o*-Cl<sub>4</sub>SQ)<sub>3</sub> was prepared at room temperature without irradiation. Successive recrystallizations from benzene resulted in tetragonal crystals of the tetrabenzene solvate, Fe(*o*-Cl<sub>4</sub>SQ)<sub>3</sub>·4C<sub>6</sub>H<sub>6</sub>. The 3,5-di(*tert*-butyl)benzosemiquinone complex was prepared by refluxing Fe(CO)<sub>5</sub> in a cyclohexane solution containing the quinone; this compound was unsolvated. All three iron complexes are dark green. Yields in all synthetic procedures were greater than 60%.

**Structure Determination of Fe(phenSQ)<sub>3</sub>·phenQ.** Preliminary photographs taken on crystals of Fe(O<sub>2</sub>C<sub>14</sub>H<sub>4</sub>)<sub>3</sub>·O<sub>2</sub>C<sub>14</sub>H<sub>8</sub> indicated triclinic symmetry. A crystal of dimensions 0.07 × 0.31 × 0.47 mm was mounted and centered on a Syntex PT automated diffractometer equipped with a graphite-crystal monochromator. The settings of 15 reflections with  $2\theta$  values greater than 19° (Mo K $\alpha$  radiation) were used to calculate the cell constants given in Table I. A complete set of intensity data was collected within the angular range  $2^\circ \leq 2\theta \leq 45^\circ$ . Symmetrical  $\theta$ - $2\theta$  scans were used within the angular range  $\pm 0.7^\circ$  on either side of the Mo K $\alpha_1$ -K $\alpha_2$  doublet at a scan rate of 4°/min. Four standard reflections measured after every 96 reflections showed normal variations in intensity during data collection. A total of 5280 reflections were measured and corrected for Lorentz, polarization, and absorption effects.

Standard "heavy atom" procedures were used to solve the structure. Sources of scattering factors, computer programs, and calculated procedures have been noted.<sup>10</sup> Three cycles of anisotropic refinement with fixed corrections for all hydrogen atoms converged with  $R_F = 0.043$  and  $R_{wF} = 0.052$ . In all calculations only the 2712 reflections with  $F_o^2 \geq 3\sigma(F_o^2)$  were used. The final value for the standard de-

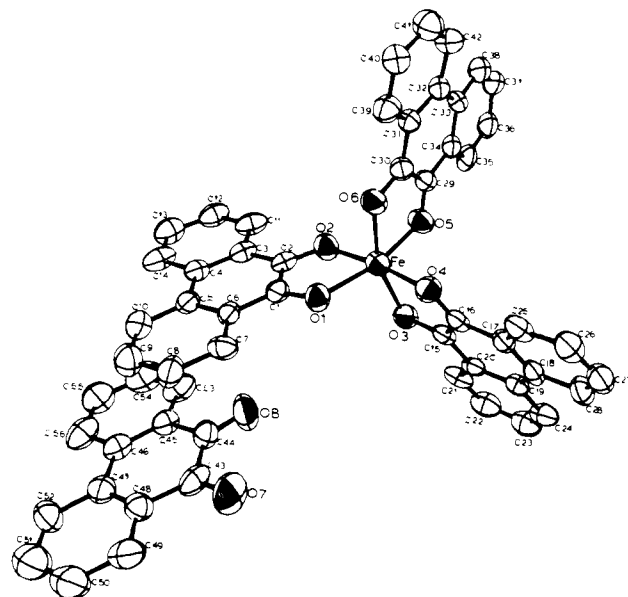


Figure 1. ORTEP plot of  $\text{Fe}(\text{phenSQ})_3 \cdot \text{phenQ}$ . Hydrogen atoms are not shown.

viation of an observation of unit weight was 1.52. The final positional and thermal parameters for  $\text{Fe}(\text{phenSQ})_3 \cdot \text{phenQ}$  are listed in Table II. Values of  $10|F_o|$  and  $10|F_c|$  (in electrons) are available in the Supplementary Material.

**Physical Measurements.** Variable-temperature magnetic susceptibility data were measured with a PAR Model 150A vibrating-sample magnetometer as indicated previously.<sup>11</sup> All data were corrected for the background and for the diamagnetism of the sample.

Iron-57 Mössbauer data were collected as before.<sup>12</sup> Isomer shifts are quoted relative to iron metal. Voltammetric measurements were made on a PAR Model 174A potentiostat.

## Results and Discussion

**Description of the Structure of  $\text{Fe}(\text{phenSQ})_3 \cdot \text{phenQ}$  and Related Molecules.** Characterization of the complexes obtained from the metal carbonyl-orthoquinone reactions has been complicated by their strong tendency to form solvates which are often nonstoichiometric. Frequently, the problem becomes one of finding a solvent or complexing agent which gives a stable, stoichiometric, and, ideally, crystalline sample. In the case of the vanadium, chromium, and iron complexes formed from tetrachloro-1,2-benzoquinone,  $\text{M}(\text{o-Cl}_4\text{SQ})_3$ , crystalline samples of formula  $\text{M}(\text{o-Cl}_4\text{SQ})_3 \cdot 4\text{C}_6\text{H}_6$  may be obtained from benzene solution. X-ray data obtained on these compounds indicate that they are isomorphous and the complex molecules isostructural. At room temperature they lose solvent with subsequent decay of their crystallinity and erratic chemical analysis. The X-ray structure determination on  $\text{Cr}(\text{o-Cl}_4\text{SQ})_3$  has been reported for the more stable  $\text{CS}_2 \cdot \text{C}_6\text{H}_6$  solvate obtained by recrystallization from  $\text{CS}_2$  solution.<sup>13</sup>

The photochemical reaction between  $\text{Fe}(\text{CO})_5$  and 9,10-phenanthrenequinone gives a highly crystalline product with four quinone moieties per iron ion. Our structural analysis of this compound indicates that the crystal structure consists of weakly interacting  $\text{Fe}(\text{phenSQ})_3$  complex molecules and molecules of unreduced quinone. A view of the  $\text{Fe}(\text{phenSQ})_3 \cdot \text{phenQ}$  pair is shown in Figure 1. Figure 2 shows the two types of intermolecular interactions which stabilize the crystal lattice. There are four-membered stacks consisting of ligands of two complex molecules above and below a pair of quinone molecules located about a crystallographic inversion center. Ligands of adjacent complex molecules are also paired directly by an inversion center located in the vicinity of the complex.

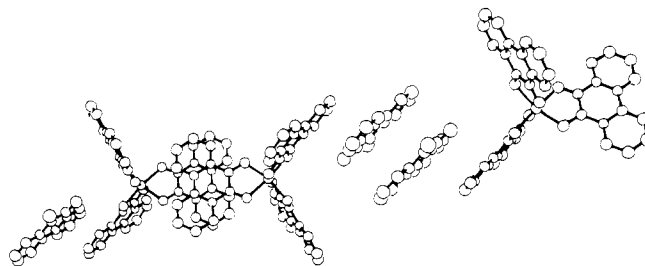


Figure 2. ORTEP plot showing the intermolecular interactions in  $\text{Fe}(\text{phenSQ})_3 \cdot \text{phenQ}$ .

Table I. Crystal Data for  $\text{Fe}(\text{O}_2\text{C}_{14}\text{H}_8)_3 \cdot \text{O}_2\text{C}_{14}\text{H}_8$

$a = 8.832 (1) \text{ \AA}$	space group $P\bar{1}$
$b = 15.621 (3) \text{ \AA}$	$Z = 2$
$c = 16.475 (3) \text{ \AA}$	mol wt 888.711
$\alpha = 117.36 (1)^\circ$	$d(\text{calcd}) = 1.465 \text{ g cm}^{-3}$
$\beta = 91.84 (1)^\circ$	$d(\text{exptl}) = 1.45 \text{ g cm}^{-3}$
$\gamma = 91.75 (1)^\circ$	$\mu = 4.52 \text{ cm}^{-1}$
$V = 2015.06 \text{ \AA}^3$	transmission coeff max = 0.968,
	min = 0.878

Interplanar separations within the four-membered stack are 3.4–3.5 Å; the interligand separation is 3.35 Å.

Isolation of the mixed complex-quinone pair is particularly fortuitous because it permits direct comparison of quinone and ligand bonding parameters. Bond distances and angles for  $\text{Fe}(\text{phenSQ})_3 \cdot \text{phenQ}$  are contained in Table III. While there has been no structural work reported for 9,10-phenanthrenequinone, we have recently reported the structure of  $\text{MoO}_2 \cdot \text{Cl}_2(\text{phenQ})$ ,<sup>14</sup> a complex of the unreduced quinone. Bonding parameters of the ligand in this molecule compare quite favorably with those of the free quinone in the present structure.

Structural differences between the quinone and the ligands of  $\text{Fe}(\text{phenSQ})_3$  are quite substantial. The C–C lengths between carbonyl carbon atoms of the ligands average to a value of 1.435 (6) Å, 0.1 Å shorter than the length in the quinone. A parameter which is still more diagnostic of the extent of ligand reduction is the C–O length. The average C–O length for the three ligands is 1.283 (3) Å, 0.070 Å longer than the values observed for the quinone. This value, however, remains significantly shorter than values of 1.349 (3), 1.349 (3), and 1.343 (10) Å found in the respective catecholate structures  $\text{Fe}(\text{O}_2\text{C}_6\text{H}_4)_3^{3-}$ ,<sup>14</sup>  $\text{Cr}(\text{O}_2\text{C}_6\text{H}_4)_3^{3-}$ ,<sup>15</sup> and  $\text{Pd}(\text{PPh}_3)_2 \cdot (\text{O}_2\text{C}_6\text{Cl}_4)$ .<sup>16</sup> In fact, the C–O lengths in  $\text{Fe}(\text{phenSQ})_3 \cdot \text{phenQ}$  are intermediate in value between the corresponding lengths found in  $\text{MoO}_2 \cdot \text{Cl}_2(\text{phenQ})$ <sup>14</sup> and those of the fully reduced ligands in  $\text{Mo}(\text{phenQ})_3$ .<sup>17</sup> They compare favorably with values of 1.31 Å found for the radical-anion ligands in  $\text{Mo}_2\text{O}_5 \cdot (\text{phenSQ})_2$ . These structural features, together with the magnetic properties of the complex (vide infra), suggest a radical-anion formulation for the quinone ligands with a high-spin ferric iron center. Complexes of ferric ion with oxygen donor ligands have characteristic Fe–O lengths which are generally close to 2.0 Å. Values of 1.992 (6), 2.008 (3), and 2.015 (6) Å, respectively, have been reported for  $\text{Fe}(\text{acac})_3$ ,<sup>18</sup>  $\text{Fe}(\text{trop})_3$ ,<sup>19</sup> and  $\text{Fe}(\text{O}_2\text{C}_6\text{H}_4)_3^{3-}$ .<sup>15</sup> The value of 2.027 (4) Å found in  $\text{Fe}(\text{phenSQ})_3$  is quite comparable with the value reported for the catecholate structure despite the three-electron difference.

In Table IV, the molecular dimensions of the chelate rings of the Cr and Fe semiquinone complexes are compared with those of the two corresponding catecholate structures. The bite angles of the semiquinone ligands are approximately 2° smaller than the angles formed by the catecholate ligands at the metal centers. Metal–oxygen lengths within this series are shortest

Table II. Positional and Thermal Parameters for the Atoms of  $\text{Fe}(\text{O}_2\text{C}_{14}\text{H}_8)_3 \cdot \text{O}_2\text{C}_{14}\text{H}_8$ 

atom	$x^a$	$y$	$z$	$B_{11}^b$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Fe	0.22538 (10)	-0.13934 (6)	0.20311 (6)	4.58 (6)	4.10 (5)	4.55 (6)	0.57 (4)	0.06 (4)	2.42 (5)
O1	0.1839 (4)	-0.2701 (2)	0.1967 (2)	3.9 (3)	4.2 (2)	5.7 (3)	0.9 (2)	1.4 (2)	2.5 (2)
O2	0.4330 (4)	-0.1963 (2)	0.1712 (2)	4.8 (3)	4.2 (3)	5.9 (3)	0.1 (2)	0.9 (3)	2.8 (2)
C1	0.2995 (5)	-0.3235 (4)	0.1754 (3)	2.8 (4)	3.7 (4)	3.6 (4)	0.6 (3)	0.6 (3)	1.7 (3)
C2	0.4351 (6)	-0.2838 (4)	0.1589 (3)	4.0 (4)	4.3 (5)	2.6 (4)	0.4 (3)	0.7 (3)	1.3 (3)
C3	0.5670 (6)	-0.3411 (4)	0.1296 (3)	3.4 (4)	4.8 (5)	3.0 (3)	0.3 (3)	0.4 (3)	1.5 (3)
C4	0.5603 (5)	-0.4355 (4)	0.1208 (3)	3.0 (3)	4.4 (5)	3.2 (3)	0.7 (3)	0.2 (3)	1.9 (3)
C5	0.4220 (6)	-0.4748 (4)	0.1412 (3)	3.8 (4)	3.5 (5)	3.0 (3)	0.7 (3)	0.4 (3)	1.3 (3)
C6	0.2923 (5)	-0.4193 (4)	0.1682 (3)	3.6 (3)	3.0 (3)	2.7 (4)	0.4 (3)	0.2 (3)	0.9 (3)
C7	0.1607 (6)	-0.4553 (4)	0.1888 (4)	4.3 (4)	4.5 (4)	4.0 (5)	-0.6 (3)	0.6 (4)	2.4 (4)
C8	0.1551 (6)	-0.5460 (4)	0.1824 (4)	5.1 (5)	3.6 (5)	5.4 (5)	0.7 (3)	1.3 (4)	1.5 (4)
C9	0.2823 (7)	-0.6015 (4)	0.1567 (4)	5.5 (5)	4.0 (5)	6.1 (4)	-0.0 (3)	0.5 (4)	2.1 (4)
C10	0.4131 (6)	-0.5663 (4)	0.1367 (4)	5.2 (5)	3.8 (5)	4.4 (4)	0.2 (3)	0.3 (3)	1.4 (4)
C11	0.6999 (6)	-0.3032 (4)	0.1094 (4)	3.0 (4)	7.5 (5)	4.0 (4)	-0.2 (4)	0.6 (4)	2.4 (4)
C12	0.8242 (6)	-0.3587 (5)	0.0807 (4)	3.7 (5)	7.0 (5)	4.3 (5)	0.6 (4)	0.9 (4)	2.2 (4)
C13	0.8174 (7)	-0.4519 (5)	0.0702 (4)	4.4 (5)	7.3 (6)	5.1 (4)	1.5 (4)	0.6 (3)	2.5 (5)
C14	0.6883 (6)	-0.4894 (5)	0.0896 (4)	3.4 (4)	7.7 (6)	3.5 (3)	1.2 (4)	0.3 (2)	2.2 (4)
O3	0.2695 (4)	-0.0586 (2)	0.3384 (2)	3.5 (2)	5.1 (5)	4.5 (3)	0.9 (2)	0.6 (2)	2.7 (2)
O4	0.0164 (4)	-0.0928 (2)	0.2433 (2)	4.2 (2)	4.5 (3)	3.9 (4)	0.5 (2)	0.0 (3)	1.9 (2)
C15	0.1595 (5)	-0.0069 (4)	0.3792 (4)	3.1 (3)	4.2 (3)	4.0 (4)	0.4 (3)	0.3 (4)	3.0 (4)
C16	0.0175 (5)	-0.0269 (4)	0.3271 (4)	2.9 (3)	3.8 (4)	4.3 (4)	0.2 (3)	0.3 (3)	3.0 (4)
C17	-0.1124 (5)	0.0279 (4)	0.3675 (4)	3.2 (3)	3.6 (4)	4.0 (4)	0.5 (3)	0.4 (4)	2.4 (4)
C18	-0.0971 (6)	0.1037 (4)	0.4574 (4)	3.8 (4)	2.9 (4)	4.6 (4)	0.3 (3)	0.2 (4)	2.4 (4)
C19	0.0470 (6)	0.1239 (4)	0.5114 (4)	3.8 (4)	3.3 (4)	3.9 (4)	0.0 (3)	0.6 (4)	2.2 (3)
C20	0.1733 (6)	0.0687 (4)	0.4729 (3)	4.5 (5)	3.1 (4)	2.9 (4)	-0.5 (3)	0.1 (4)	1.9 (3)
C21	0.3118 (6)	0.0869 (4)	0.5241 (4)	4.6 (4)	5.1 (4)	4.2 (5)	-1.5 (3)	-1.4 (4)	3.4 (4)
C22	0.3264 (7)	0.1596 (5)	0.6116 (4)	5.9 (5)	5.6 (5)	4.8 (4)	-1.5 (4)	-1.1 (4)	2.9 (5)
C23	0.2040 (8)	0.2132 (4)	0.6503 (4)	7.4 (6)	4.8 (5)	4.3 (5)	-1.2 (4)	-0.6 (5)	2.2 (4)
C24	0.0670 (7)	0.1968 (4)	0.6023 (4)	6.7 (5)	4.2 (4)	3.5 (4)	-0.8 (4)	-0.3 (4)	2.2 (4)
C25	-0.2529 (6)	0.0065 (4)	0.3178 (4)	3.4 (4)	5.4 (5)	5.5 (4)	0.0 (3)	0.1 (4)	4.0 (4)
C26	-0.3756 (6)	0.0611 (4)	0.3547 (4)	3.7 (4)	5.5 (5)	6.6 (6)	0.3 (4)	0.4 (4)	3.9 (5)
C27	-0.3568 (6)	0.1381 (4)	0.4424 (4)	4.6 (5)	5.3 (5)	6.9 (6)	1.2 (4)	1.5 (4)	4.0 (5)
C28	-0.2225 (6)	0.1590 (4)	0.4925 (4)	3.8 (4)	4.8 (5)	6.0 (5)	1.2 (3)	0.5 (4)	3.3 (4)
O5	0.3087 (4)	-0.0255 (2)	0.1866 (2)	5.7 (3)	3.8 (2)	4.3 (3)	-0.5 (2)	-0.5 (2)	2.1 (2)
O6	0.1464 (4)	-0.1782 (2)	0.0728 (2)	6.2 (3)	3.8 (2)	4.2 (3)	-0.1 (2)	0.2 (2)	2.1 (2)
C29	0.2741 (6)	-0.0325 (4)	0.1079 (3)	3.9 (4)	1.1 (4)	3.2 (4)	0.3 (3)	-0.0 (3)	1.5 (3)
C30	0.1803 (6)	-0.1159 (4)	0.0458 (3)	3.9 (4)	3.8 (5)	4.1 (4)	0.6 (3)	1.1 (4)	2.1 (4)
C31	0.1227 (6)	-0.1235 (4)	-0.0403 (4)	4.1 (4)	3.5 (4)	3.8 (4)	0.8 (3)	1.0 (3)	2.0 (3)
C32	0.1661 (6)	-0.0514 (4)	-0.0652 (4)	4.4 (4)	3.1 (4)	3.9 (4)	0.9 (3)	0.9 (4)	1.8 (3)
C33	0.2772 (6)	0.0281 (4)	-0.0058 (4)	5.0 (4)	2.8 (4)	3.6 (4)	0.6 (3)	0.7 (4)	1.8 (3)
C34	0.3285 (6)	0.0377 (4)	0.0799 (4)	4.8 (4)	2.8 (4)	3.9 (4)	1.0 (3)	1.2 (4)	1.6 (3)
C35	0.4331 (6)	0.1122 (4)	0.1363 (4)	5.1 (4)	2.1 (4)	4.7 (4)	-0.6 (3)	1.0 (4)	0.7 (3)
C36	0.4895 (7)	0.1761 (4)	0.1064 (4)	6.3 (5)	3.1 (4)	5.2 (5)	0.8 (3)	1.2 (4)	1.6 (4)
C37	0.4419 (7)	0.1663 (4)	0.0223 (4)	7.8 (6)	3.1 (5)	4.2 (5)	0.9 (4)	1.1 (4)	1.4 (4)
C38	0.3377 (7)	0.0946 (4)	-0.0327 (4)	6.5 (5)	3.5 (5)	4.7 (4)	0.5 (4)	0.8 (4)	1.8 (4)
C39	0.0210 (6)	-0.1994 (4)	-0.0968 (4)	4.3 (4)	4.6 (5)	3.9 (4)	0.2 (3)	-0.3 (4)	1.6 (4)
C40	-0.0381 (7)	-0.2046 (4)	-0.1768 (4)	6.0 (5)	4.6 (5)	4.8 (5)	0.9 (4)	0.6 (4)	2.2 (4)
C41	0.0022 (7)	-0.1341 (4)	-0.2019 (4)	6.0 (5)	5.1 (5)	5.5 (5)	-0.3 (4)	-0.3 (4)	2.6 (5)
C42	0.1016 (7)	-0.0576 (4)	-0.1468 (4)	6.0 (4)	5.7 (5)	4.0 (5)	1.0 (4)	0.3 (4)	2.3 (4)
O7	0.1567 (5)	-0.4226 (3)	0.4383 (3)	6.2 (4)	8.1 (4)	12.1 (5)	3.2 (3)	3.8 (4)	5.0 (4)
O8	0.3930 (5)	-0.3534 (3)	0.3828 (3)	7.9 (4)	4.7 (3)	9.6 (4)	1.5 (3)	1.2 (3)	3.9 (3)
C43	0.2670 (6)	-0.4704 (4)	0.4136 (4)	3.9 (5)	5.9 (5)	4.7 (5)	1.7 (4)	1.2 (4)	1.8 (4)
C44	0.4051 (7)	-0.4288 (4)	0.3863 (4)	5.8 (4)	3.6 (5)	4.2 (4)	0.3 (4)	0.1 (4)	1.4 (4)
C45	0.5418 (6)	-0.4832 (4)	0.3632 (4)	4.1 (4)	4.6 (5)	3.9 (4)	0.4 (4)	0.3 (3)	1.9 (4)
C46	0.5458 (6)	-0.5738 (4)	0.3605 (4)	3.9 (4)	4.9 (5)	3.9 (4)	0.4 (3)	0.3 (3)	1.9 (4)
C47	0.4133 (6)	-0.6165 (4)	0.3833 (4)	4.1 (3)	4.2 (1)	4.5 (3)	0.0 (2)	0.4 (2)	2.0 (4)
C48	0.2782 (6)	-0.5671 (4)	0.4089 (4)	4.9 (5)	4.4 (5)	4.2 (4)	0.3 (4)	-0.2 (4)	2.4 (4)
C49	0.1544 (7)	-0.6053 (5)	0.4341 (4)	6.2 (5)	6.6 (6)	4.5 (5)	-0.5 (4)	0.8 (4)	2.6 (4)
C50	0.1590 (8)	-0.6947 (5)	0.4306 (5)	8.6 (7)	6.7 (6)	6.0 (6)	-1.5 (5)	-0.0 (5)	3.7 (5)
C51	0.2894 (9)	-0.7455 (5)	0.4030 (5)	8.6 (7)	6.9 (6)	6.4 (6)	0.9 (5)	-0.5 (4)	3.8 (5)
C52	0.4107 (8)	-0.7071 (4)	0.3801 (4)	8.4 (6)	4.4 (5)	5.1 (5)	0.0 (4)	-0.5 (4)	2.8 (4)
C53	0.6676 (7)	-0.4422 (5)	0.3434 (4)	4.7 (5)	6.8 (5)	5.5 (5)	-0.0 (4)	0.9 (4)	2.0 (5)
C54	0.7988 (8)	-0.4899 (6)	0.3207 (5)	5.6 (6)	9.3 (8)	7.1 (7)	-0.0 (5)	1.1 (5)	3.2 (6)
C55	0.8050 (7)	-0.5800 (5)	0.3171 (5)	5.2 (5)	7.3 (7)	7.7 (6)	1.1 (5)	1.3 (4)	3.6 (6)
C56	0.6890 (7)	-0.6216 (5)	0.3363 (4)	4.7 (5)	6.6 (6)	5.2 (5)	1.3 (4)	0.5 (4)	1.7 (4)

<sup>a</sup> Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. <sup>b</sup> The form of the anisotropic thermal ellipsoid is  $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^{*}b^{*} + 2B_{13}hla^{*}c^{*} + 2B_{23}klb^{*}c^{*})]$  and is given in units of  $\text{\AA}^2$ .

for  $\text{Cr}(o\text{-Cl}_4\text{SQ})_3$  and longest for  $\text{Fe}(\text{phenSQ})_3$ . This has a direct bearing on the solution chemistry of the Cr and Fe

semiquinone complexes. The ligands in the  $\text{Cr}^{3+}$  complexes are more tightly bound to the metal and much less subject to

Table III. Bonding Parameters for the Fe(phenSQ)<sub>3</sub> Complex Molecule and 9,10-Phenanthrenequinone

Inner Coordination Sphere (Å)				Ligand I (Å)			
Fe-O(1)	2.018 (3)	Fe-O(4)	2.023 (3)	C(1)-O(1)	1.292 (5)	C(7)-C(8)	1.370 (7)
Fe-O(2)	2.040 (3)	Fe-O(5)	2.037 (3)	C(2)-O(2)	1.286 (5)	C(8)-C(9)	1.395 (7)
Fe-O(3)	2.011 (3)	Fe-O(6)	2.035 (3)	C(1)-C(2)	1.423 (6)	C(9)-C(10)	1.377 (7)
Angles (deg)				C(2)-C(3)	1.447 (7)	C(5)-C(10)	1.397 (7)
O(1)-Fe-O(2)	79.2 (1)	O(2)-Fe-O(4)	172.7 (1)	C(3)-C(4)	1.412 (7)	C(3)-C(11)	1.416 (6)
O(3)-Fe-O(4)	79.6 (1)	O(2)-Fe-O(5)	87.5 (1)	C(4)-C(5)	1.468 (6)	C(11)-C(12)	1.377 (7)
O(5)-Fe-O(6)	79.4 (1)	O(2)-Fe-O(6)	97.0 (1)	C(5)-C(6)	1.414 (6)	C(12)-C(13)	1.385 (8)
O(1)-Fe-O(3)	100.4 (1)	O(3)-Fe-O(5)	87.8 (1)	C(1)-C(6)	1.445 (6)	C(13)-C(14)	1.379 (7)
O(1)-Fe-O(4)	94.6 (1)	O(3)-Fe-O(6)	160.0 (1)	C(6)-C(7)	1.394 (6)	C(4)-C(14)	1.396 (7)
O(1)-Fe-O(5)	165.2 (1)	O(4)-Fe-O(5)	99.0 (1)	Angles (deg)			
O(1)-Fe-O(6)	95.6 (1)	O(4)-Fe-O(6)	87.3 (1)	Fe-O(1)-C(1)	113.8 (3)	C(14)-C(13)-C(12)	120.8 (6)
O(2)-Fe-O(3)	97.7 (1)			Fe-O(2)-C(2)	113.2 (3)	C(13)-C(12)-C(11)	119.7 (5)
				C(3)-C(4)-C(5)	120.6 (4)	C(9)-C(10)-C(3)	119.8 (6)
				C(4)-C(5)-C(6)	120.3 (4)	C(11)-C(3)-C(4)	120.7 (5)
				C(2)-C(1)-C(6)	121.2 (4)	C(5)-C(6)-C(7)	120.9 (5)
				C(1)-C(6)-C(5)	118.6 (4)	C(6)-C(7)-C(8)	120.1 (5)
				C(3)-C(4)-C(14)	117.2 (5)	C(7)-C(8)-C(9)	119.8 (5)
				C(4)-C(14)-C(13)	121.7 (6)	C(8)-C(9)-C(10)	120.6 (6)
				C(3)-C(4)-C(5)	120.6 (4)	C(9)-C(10)-C(5)	121.2 (5)
				C(4)-C(5)-C(6)	120.3 (4)	C(10)-C(5)-C(6)	117.4 (4)
				C(2)-C(1)-C(6)	121.2 (4)	C(2)-C(3)-C(11)	120.2 (5)
				C(1)-C(6)-C(5)	118.6 (4)	C(1)-C(6)-C(7)	120.4 (5)
				C(3)-C(4)-C(14)	117.2 (5)	C(14)-C(4)-C(5)	122.2 (5)
				C(4)-C(14)-C(13)	121.7 (6)	C(10)-C(5)-C(4)	122.2 (5)
				Ligand II (Å)			
				C(15)-O(3)	1.280 (5)	C(21)-C(22)	1.364 (7)
				C(16)-O(4)	1.287 (5)	C(22)-C(23)	1.373 (8)
				C(15)-C(16)	1.438 (6)	C(23)-C(24)	1.374 (7)
				C(16)-C(17)	1.441 (7)	C(24)-C(19)	1.405 (7)
				C(17)-C(18)	1.407 (6)	C(17)-C(25)	1.407 (6)
				C(18)-C(19)	1.469 (7)	C(25)-C(26)	1.376 (7)
				C(19)-C(20)	1.412 (6)	C(26)-C(27)	1.392 (7)
				C(20)-C(15)	1.447 (6)	C(27)-C(28)	1.364 (7)
				C(20)-C(21)	1.408 (6)	C(28)-C(18)	1.396 (6)
				Angles (deg)			
Fe-O(3)-C(15)	113.1 (3)	C(28)-C(27)-C(26)	122.0 (5)	O(7)-C(43)-C(44)	118.6 (6)	C(51)-C(50)-C(49)	118.9 (6)
Fe-O(4)-C(16)	112.8 (3)	C(27)-C(26)-C(25)	118.1 (5)	O(7)-C(43)-C(48)	123.7 (5)	C(50)-C(49)-C(48)	120.4 (6)
C(3)-C(15)-C(16)	116.7 (5)	C(26)-C(25)-C(17)	120.9 (5)	O(8)-C(44)-C(43)	118.2 (5)	C(49)-C(48)-C(47)	121.3 (5)
O(3)-C(15)-C(20)	123.1 (4)	C(25)-C(17)-C(18)	120.1 (5)	O(8)-C(44)-C(45)	123.3 (5)	C(45)-C(46)-C(56)	117.4 (5)
O(4)-C(16)-C(15)	116.3 (4)	C(19)-C(20)-C(21)	120.8 (5)	C(43)-C(44)-C(45)	118.5 (5)	C(46)-C(56)-C(55)	120.9 (6)
O(4)-C(16)-C(17)	123.2 (4)	C(20)-C(21)-C(22)	120.2 (5)	C(44)-C(45)-C(46)	121.2 (5)	C(56)-C(55)-C(54)	120.7 (6)
				C(45)-C(46)-C(47)	121.2 (5)	C(55)-C(54)-C(53)	119.4 (6)
				C(46)-C(47)-C(48)	120.9 (5)	C(54)-C(53)-C(45)	120.5 (6)
				C(47)-C(48)-C(43)	120.4 (5)	C(53)-C(45)-C(46)	121.1 (5)
				C(48)-C(43)-C(44)	117.6 (5)	C(43)-C(48)-C(49)	118.2 (5)
				C(48)-C(47)-C(52)	115.6 (5)	C(44)-C(45)-C(53)	117.7 (5)
				C(47)-C(52)-C(51)	123.2 (6)	C(47)-C(46)-C(56)	121.4 (5)
				C(52)-C(51)-C(50)	120.3 (7)	C(46)-C(47)-C(52)	123.4 (5)
				9,10-Phenanthrenequinone (Å)			
				C(29)-O(5)	1.278 (5)	C(35)-C(36)	1.387 (7)
				C(30)-O(6)	1.274 (5)	C(36)-C(37)	1.372 (7)
				C(29)-C(30)	1.444 (7)	C(37)-C(38)	1.370 (7)
				C(30)-C(31)	1.442 (6)	C(38)-C(33)	1.401 (7)
				C(31)-C(32)	1.412 (6)	C(31)-C(39)	1.395 (7)
				C(32)-C(33)	1.487 (7)	C(39)-C(40)	1.368 (7)
				C(33)-C(34)	1.408 (7)	C(40)-C(41)	1.383 (7)
				C(34)-C(29)	1.445 (7)	C(41)-C(42)	1.382 (7)
				C(34)-C(35)	1.399 (7)	C(32)-C(42)	1.403 (7)
				Angles (deg)			
				Fe-O(5)-C(29)	113.3 (3)	C(42)-C(41)-C(40)	120.9 (6)
				Fe-O(6)-C(30)	113.3 (3)	C(41)-C(40)-C(39)	120.0 (6)
				O(5)-C(29)-C(30)	116.8 (4)	C(40)-C(39)-C(31)	120.4 (5)
				O(5)-C(29)-C(34)	122.4 (4)	C(39)-C(31)-C(32)	120.3 (5)
				O(6)-C(30)-C(29)	117.0 (5)	C(33)-C(34)-C(35)	120.7 (5)
				O(6)-C(30)-C(31)	122.8 (5)	C(34)-C(35)-C(36)	119.5 (5)
				C(29)-C(30)-C(31)	120.0 (5)	C(35)-C(36)-C(37)	120.0 (5)
				C(30)-C(31)-C(32)	119.3 (5)	C(36)-C(37)-C(38)	120.9 (5)
				C(31)-C(32)-C(33)	120.1 (5)	C(37)-C(38)-C(33)	121.3 (5)
				C(32)-C(33)-C(34)	120.3 (4)	C(38)-C(33)-C(34)	117.4 (5)
				C(33)-C(34)-C(29)	118.8 (5)	C(29)-C(34)-C(35)	120.4 (5)
				C(34)-C(29)-C(30)	120.7 (4)	C(30)-C(31)-C(38)	120.4 (5)
				C(31)-C(32)-C(42)	118.1 (5)	C(32)-C(33)-C(38)	122.2 (5)
				C(32)-C(42)-C(41)	120.3 (5)	C(33)-C(32)-C(42)	121.8 (5)
				9,10-Phenanthrenequinone (Å)			
				C(43)-O(7)	1.210 (6)	C(49)-C(50)	1.372 (8)
				C(44)-O(8)	1.212 (6)	C(50)-C(51)	1.386 (9)
				C(43)-C(44)	1.539 (7)	C(51)-C(52)	1.358 (8)
				C(44)-C(45)	1.456 (7)	C(52)-C(47)	1.391 (7)
				C(45)-C(46)	1.397 (7)	C(45)-C(53)	1.387 (7)
				C(46)-C(47)	1.472 (7)	C(53)-C(54)	1.364 (8)
				C(47)-C(48)	1.410 (7)	C(54)-C(55)	1.384 (9)
				C(48)-C(43)	1.483 (7)	C(55)-C(56)	1.375 (8)
				C(48)-C(49)	1.394 (7)	C(56)-C(46)	1.397 (7)
				Angles (deg)			
				O(7)-C(43)-C(44)	118.6 (6)	C(51)-C(50)-C(49)	118.9 (6)
				O(7)-C(43)-C(48)	123.7 (5)	C(50)-C(49)-C(48)	120.4 (6)
				O(8)-C(44)-C(43)	118.2 (5)	C(49)-C(48)-C(47)	121.3 (5)
				O(8)-C(44)-C(45)	123.3 (5)	C(45)-C(46)-C(56)	117.4 (5)
				C(43)-C(44)-C(45)	118.5 (5)	C(46)-C(56)-C(55)	120.9 (6)
				C(44)-C(45)-C(46)	121.2 (5)	C(56)-C(55)-C(54)	120.7 (6)
				C(45)-C(46)-C(47)	121.2 (5)	C(55)-C(54)-C(53)	119.4 (6)
				C(46)-C(47)-C(48)	120.9 (5)	C(54)-C(53)-C(45)	120.5 (6)
				C(47)-C(48)-C(43)	120.4 (5)	C(53)-C(45)-C(46)	121.1 (5)
				C(48)-C(43)-C(44)	117.6 (5)	C(43)-C(48)-C(49)	118.2 (5)
				C(48)-C(47)-C(52)	115.6 (5)	C(44)-C(45)-C(53)	117.7 (5)
				C(47)-C(52)-C(51)	123.2 (6)	C(47)-C(46)-C(56)	121.4 (5)
				C(52)-C(51)-C(50)	120.3 (7)	C(46)-C(47)-C(52)	123.4 (5)

dissociation than ligands in the ferric complexes. We have examined voltammetrically the Fe and Cr semiquinone complexes formed from the three different quinones, 3,5 di(*tert*-butyl)-1,2-benzoquinone, tetrachloro-1,2-benzoquinone, and 9,10-phenanthrenequinone. The Fe complexes show only irreversible reductions and, after a period of approximately 1 h, the redox half-waves associated with the free quinone. The Cr complexes, however, exhibit six reversible or quasi-reversible half-waves corresponding to members of the series Cr(quinone)<sub>3</sub><sup>3+</sup> to Cr(cat)<sub>3</sub><sup>3-</sup>. Through this redox series the metal remains essentially trivalent while electrons are added

to or removed from levels which are primarily ligand in character.<sup>20</sup> It is the kinetic stability of Cr<sup>3+</sup> which appears responsible for this redox series.

**<sup>57</sup>Fe Mössbauer Spectroscopy.** The Mössbauer spectrum of an iron compound is useful in determining the oxidation state and spin state of the metal. Spectra were obtained at 90 K for the three Fe(SQ)<sub>3</sub> complexes. In each case, the spectrum consists of a single quadrupole-split doublet. The spectra of Fe(3,5-DBSQ)<sub>3</sub> and Fe(*o*-Cl<sub>4</sub>SQ)<sub>3</sub>·4Ph are illustrated in Figure 3. Each doublet was least-squares fit with two Lorentzian lines, each constrained to have the same area. The

Table IV. Bonding Parameters within the Chelate Rings of Semiquinone and Catecholate Complexes of Cr and Fe

	Cr(O <sub>2</sub> C <sub>6</sub> Cl <sub>4</sub> ) <sub>3</sub>	Cr(O <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> <sup>3-</sup>	Fe(O <sub>2</sub> C <sub>14</sub> H <sub>8</sub> ) <sub>3</sub>	Fe(O <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> <sup>3-</sup>
M-O, Å	1.949 (5)	1.986 (4)	2.027 (4)	2.015 (6)
C-O, Å	1.28 (1)	1.349 (3)	1.283 (3)	1.349 (3)
C-C, Å	1.44 (1)	1.411 (4)	1.435 (6)	1.409 (4)
O-M-O, deg	81.8 (2)	83.6 (1)	79.4 (1)	81.3 (1)
M-O-C, deg	113.3 (5)	110.7 (2)	113.3 (3)	112.0 (4)
C-C-O, deg	115.8 (8)	117.2 (4)	116.7 (4)	118.0 (8)

Table V. Iron-57 Mössbauer Data (90 K)

compd	$\delta$ , <sup>a,b</sup> mm/s	$\Delta E_Q$ , <sup>b</sup> mm/s	$I'$ , <sup>b,c</sup> mm/s
Fe(3,5-DBSQ) <sub>3</sub>	0.559 (2)	0.752 (2)	0.140 (2)
Fe( <i>o</i> -Cl <sub>4</sub> SQ) <sub>3</sub> ·4Ph	0.536 (7)	0.940 (7)	0.201 (8)
Fe(phenSQ) <sub>3</sub> ·phenQ	0.530 (4)	0.924 (4)	0.245 (4)

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

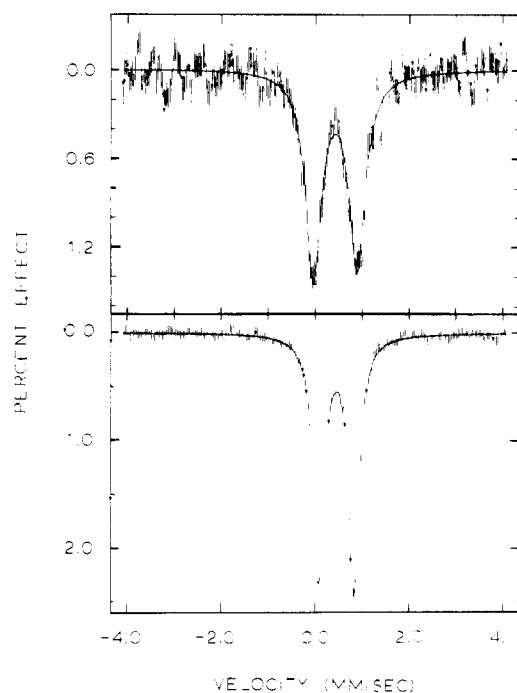


Figure 3. <sup>57</sup>Fe Mössbauer spectra for 90 K samples of Fe(*o*-Cl<sub>4</sub>SQ)<sub>3</sub>·4Ph (upper) and Fe(3,5-DBSQ)<sub>3</sub> (lower).

resulting isomer shift and quadrupole splitting data are given in Table V.

Examination of the data in Table V shows that all three Fe(SQ)<sub>3</sub> complexes give essentially the same <sup>57</sup>Fe Mössbauer data. There is one feature that does vary slightly from one compound to another. This is the degree of asymmetry in the doublet for each compound. The doublet observed for Fe(3,5-DBSQ)<sub>3</sub> is relatively symmetric, whereas the doublets for the other two compounds are slightly asymmetric. The Mössbauer data for the Fe(SQ)<sub>3</sub> complexes are consistent with the iron ion being described as high-spin iron(III).<sup>21</sup> The isomer shift ( $\delta$ ) is ca. 0.53 mm/s relative to iron metal and the quadrupole splitting ( $\Delta E_Q$ ) is ca. 0.9 mm/s.

**Magnetic Susceptibility of the Iron(III) and Chromium(III) Complexes.** Variable-temperature (4.2–285 K) magnetic susceptibility data were collected for Fe(3,5-DBSQ)<sub>3</sub>, Fe(*o*-Cl<sub>4</sub>SQ)<sub>3</sub>·4Ph, and Fe(phenSQ)<sub>3</sub>·phenQ and are presented in Tables VI, VII, and VIII, respectively.<sup>22</sup> Figure 4 illustrates the  $\mu_{\text{eff}}$  vs. temperature curves for these three iron(III) complexes.

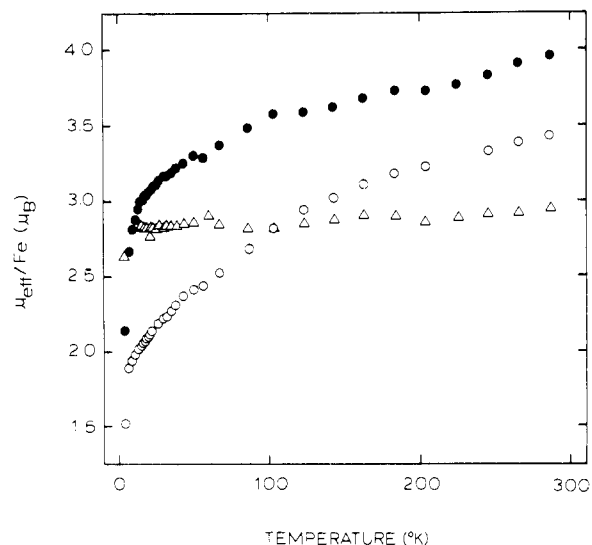
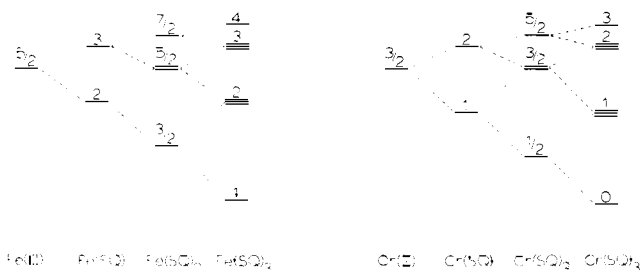


Figure 4. Plots of the effective magnetic moment ( $\mu_{\text{eff}}$ ) per iron ion as a function of temperature for Fe(3,5-DBSQ)<sub>3</sub> ( $\Delta$ ), Fe(*o*-Cl<sub>4</sub>SQ)<sub>3</sub>·4Ph ( $\bullet$ ), and Fe(phenSQ)<sub>3</sub>·phenQ ( $\circ$ ).

If the Fe(SQ)<sub>3</sub> complexes are properly formulated as tris(*o*-semiquinone) complexes of high-spin iron(III), an *intra*-molecular antiferromagnetic exchange interaction between the ligand-based unpaired electrons and the metal unpaired electrons would result in a triplet ( $S = 1$ ) ground state with two unpaired electrons. When the exchange interaction is relatively weak, there would be thermally accessible excited states. The Fe(SQ)<sub>3</sub> complex would have three  $S = 2$  energetically degenerate excited states, three  $S = 3$  energetically degenerate excited states, and one  $S = 4$  excited state. Thus, a weak antiferromagnetic interaction in Fe(SQ)<sub>3</sub> would result in the thermal population of  $S = 2, 3,$  and  $4$  excited states. This would lead to  $\mu_{\text{eff}}$  values that are very temperature dependent. The origin of the  $S = 1, 2, 3,$  and  $4$  electronic states for an Fe(SQ)<sub>3</sub> complex can be seen from an examination of Figure 5, which shows the consequence of spin coupling one  $S = 1/2$  semiquinone to the high-spin iron(III) ion with  $S = 5/2$  to give  $S = 2$  and  $3$  states for Fe(SQ)<sub>2</sub><sup>+</sup>. Coupling a second  $S = 1/2$  semiquinone antiferromagnetically to the Fe(SQ)<sub>2</sub><sup>+</sup> moiety results in one  $S = 3/2$  state, two  $S = 5/2$  states, and one  $S = 7/2$  state. And finally, the antiferromagnetic interaction of the third  $S = 1/2$  semiquinone with the Fe(SQ)<sub>2</sub><sup>+</sup> unit gives the  $S = 1, 2, 3,$  and  $4$  states for the Fe(SQ)<sub>3</sub> complex. Unfortunately, at present, the derivation of the theoretical magnetic susceptibility expression for such a species has not been presented.



**Figure 5.** The low-lying energy states for the  $M(SQ)_3$  complexes resulting from an intramolecular antiferromagnetic exchange interaction between the unpaired electrons of the *o*-semiquinone ligands and the metal ion.

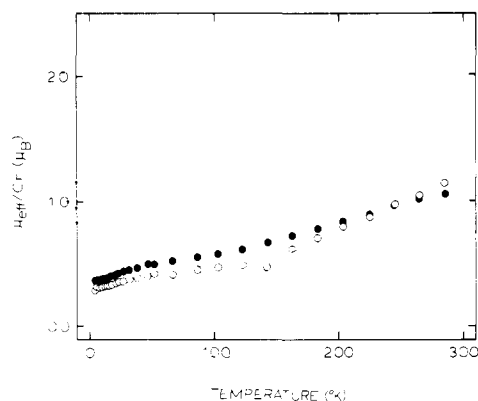
In the case of  $Fe(3,5\text{-DBSQ})_3$ , the  $\chi_M^{-1}$  vs. temperature data could be least-squares fit to a straight line to give a Curie-Weiss temperature,  $\theta$ , of  $-0.86$  K. As can be seen in Figure 4, this compound has  $\mu_{\text{eff}} = 2.95 \mu_B$  at 285 K and there is very little temperature dependence in the  $\mu_{\text{eff}}$  value down to almost 4.2 K. This  $\mu_{\text{eff}}$  value is, of course, quite close to the spin-only value for two unpaired electrons. It is clear that only the  $S = 1$  ground state is thermally populated in this complex even up to 285 K. Thus, the energy separation between this  $S = 1$  ground state and the three  $S = 2$  lowest lying excited states appreciably exceeds thermal energies at 285 K.

Perhaps the most interesting observation in this study is that the 285 K  $\mu_{\text{eff}}$  values for both  $Fe(o\text{-Cl}_4\text{SQ})_3\cdot 4\text{Ph}$  and  $Fe(\text{phenSQ})_3\cdot \text{phenQ}$  are considerably greater than the spin-only value for two unpaired electrons. Figure 4 shows that there is a marked temperature dependence in the  $\mu_{\text{eff}}$  values for these two complexes. This is all explicable in terms of a relatively weak antiferromagnetic exchange interaction between the unpaired electrons of the ligand and those of the high-spin iron(III) ion. In these two  $Fe(SQ)_3$  complexes the energy separation between the  $S = 1$  and  $S = 2$  states is within thermal energies at 285 K and there is some thermal population of the  $S = 2$  excited states.

As can be seen in Figure 4, the  $\mu_{\text{eff}}$  value for  $Fe(o\text{-Cl}_4\text{SQ})_3\cdot 4\text{Ph}$  drops to  $2.14 \mu_B$  at 4.2 K. It is suggested that very weak *intermolecular* magnetic exchange interactions between  $Fe(o\text{-Cl}_4\text{SQ})_3$  complexes result in the attenuation of  $\mu_{\text{eff}}$  below the spin-only value for two unpaired electrons. The crystal structure of this compound does show *intermolecular* contacts that could support such an extended interaction.

Substantial *intermolecular* contacts could be seen in the structure for  $Fe(\text{phenSQ})_3\cdot \text{phenQ}$  and this is in keeping with the fact that this compound shows an attenuation in  $\mu_{\text{eff}}$  even further below the two-electron spin-only value than observed for the  $o\text{-Cl}_4\text{SQ}^-$  complex. One other fact substantiates the suggestion of *intermolecular* interactions in these two  $Fe(SQ)_3$  complexes. A series of complexes with the composition  $Fe^{III}(\text{salen})(\text{SQ})$  has been prepared by the reaction of  $Fe^{II}(\text{salen})$  with an *o*-quinone.<sup>23</sup> When the semiquinone is 3,5-DBSQ<sup>-</sup>, there is little sign of an *intermolecular* antiferromagnetic interaction, whereas, when the SQ<sup>-</sup> is not sterically blocked with *tert*-butyl groups and it is large and conjugated, there are such interactions.

An explanation for the relatively weak *intramolecular* antiferromagnetic interaction observed for  $Fe(o\text{-Cl}_4\text{SQ})_3\cdot 4\text{Ph}$  and  $Fe(\text{phenSQ})_3\cdot \text{phenQ}$  is possible. The single unpaired electron of a *o*-semiquinone is located in a  $\pi$ -type molecular orbital as has been found in various molecular orbital calculations.<sup>24</sup> Superhyperfine structure seen in the EPR spectra for various *o*-semiquinones indicates that the unpaired electron density is spread throughout the molecule.<sup>25</sup> The unpaired electron of the *o*-semiquinone ligand is not directly involved in the bonding of the *o*-semiquinone to the high-spin iron(III) ion. A lone pair of electrons on each oxygen atom of the *o*-semiquinone is used in the bonding to the metal. Consequently,



**Figure 6.** Plots of the effective magnetic moment ( $\mu_{\text{eff}}$ ) per chromium ion as a function of temperature for  $Cr(o\text{-Cl}_4\text{SQ})_3\cdot 4\text{Ph}$  (●) and  $Cr(\text{phenSQ})_3\cdot \text{anisole}$  (○).

the intramolecular antiferromagnetic interaction is relatively weak. It is interesting that the weaker interactions are found for the  $o\text{-Cl}_4\text{SQ}^-$  and  $\text{phenSQ}^-$  complexes. The  $\text{phenSQ}^-$  ligand presents the greatest opportunity for delocalization of the unpaired electron density and, thus, the amount of unpaired electron density on the oxygen atoms of  $\text{phenSQ}^-$  is reduced and this reduces the interaction. The strong electron-withdrawing substituents on  $o\text{-Cl}_4\text{SQ}^-$  would have the same effect. On the other hand, the 3,5-DBSQ<sup>-</sup> ligand has electron-donating substituents and this could tend to increase the interaction. The weak antiferromagnetic coupling present in these  $Fe(SQ)_3$  is reminiscent of the ozone model proposed by Goddard<sup>26</sup> for the bonding of  $O_2$  to an iron heme. It is important to note that the two unpaired electrons found in the  $S = 1$  ground state for the  $Fe(SQ)_3$  complexes are most likely delocalized throughout the molecule. We were unable to see any credible EPR signals for powdered samples of the  $Fe(SQ)_3$  complexes maintained in the 77–300 K range. This is as expected because the  $S = 1$  ground state would be expected to be experiencing zero-field splitting that would make the EPR signal very difficult to observe.

Variable-temperature (4.2–300 K) magnetic susceptibility data were also obtained for  $Cr(o\text{-Cl}_4\text{SQ})_3\cdot 4\text{Ph}$  and  $Cr(\text{phenSQ})_3\cdot \text{phenQ}$ ; the data are collected in Tables IX and X,<sup>22</sup> respectively, and are illustrated in Figure 6. It was thought that these two chromium complexes could also be tris(*o*-semiquinone) complexes. The chromium(III) ion has three unpaired electrons and an antiferromagnetic exchange interaction with three  $X = 1/2$  semiquinones would lead to an  $S = 0$  diamagnetic ground state for such a  $Cr(SQ)_3$  complex. Figure 5 shows that, for a  $Cr(SQ)_3$  complex, there would be three energetically degenerate  $S = 1$  excited states, three energetically degenerate  $S = 2$  excited states, and one  $S = 3$  excited state.

Examination of Figure 6 shows that indeed these two  $Cr(SQ)_3$  complexes do show some residual paramagnetism at the higher temperatures. The  $\mu_{\text{eff}}$  values are temperature dependent owing to a changing Boltzmann distribution in the  $S = 0$  ground and  $S = 1$  excited states. These complexes are also tris(*o*-semiquinone) complexes. At 286 K,  $Cr(\text{phenSQ})_3\cdot \text{anisole}$  has a magnetic moment of  $1.15 \mu_B$ , which drops to a value of  $0.30 \mu_B$  at 4.2 K. Similar behavior is observed for  $Cr(o\text{-Cl}_4\text{SQ})_3\cdot 4\text{Ph}$ , where  $\mu_{\text{eff}}$  is  $1.08 \mu_B$  at 286 K and drops to a value of  $0.38 \mu_B$  at 4.2 K. The limiting low-temperature  $\mu_{\text{eff}}$  values for these two  $Cr(SQ)_3$  complexes most likely reflect the level of temperature-independent paramagnetism in these complexes. The characteristics of the two  $Cr(SQ)_3$  complexes are quite similar to those reported for  $Cr(\text{bpy})_3$  where  $\mu_{\text{eff}}$  is  $1.41 \mu_B$  at 416.8 K and decreases to  $0.52 \mu_B$  at 83.5 K.<sup>4</sup> The complex  $Cr(\text{bpy})_3$  was formulated as a chromium(III) complex

with three  $bpy^-$  radical ( $S = 1/2$ ) ligands. It is interesting that a comparable magnitude of *intra*molecular antiferromagnetic exchange interaction is present in the two types of complexes.

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**Supplementary Material Available:** Tables VI–X (experimental magnetic susceptibility data) (14 pages). Ordering information is given on any current masthead page.

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$$R_F = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$R_{wF} = \left( \frac{\sum w(F_o - |F_c|)^2}{\sum w|F_o|^2} \right)^{1/2}$$

The function minimized during refinement was  $\sum w(|F_o| - |F_c|)^2$  with weights calculated by the equation  $w = 4F_o^2/\sigma^2(F_o^2)$ .

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## Reactions of Activated Quadruply Bonded Molybdenum Dimers. Formation of New Rectangular Clusters Containing the Tetrametal Analogue of Cyclobutadiyne

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**Abstract:** A new quadruply bonded molybdenum dimer,  $Mo_2Cl_4(P(C_6H_5)_3)_2(CH_3OH)_2$ , has been prepared, characterized by structure analysis, and shown to exhibit unusual reactivity. In benzene solution the new dimer undergoes self-addition across the quadruple bond resulting in formation of a novel tetrameric cluster unit. Structure determination of the triethylphosphine substituted tetramer,  $Mo_4Cl_8(PEt_3)_4$ , revealed the molecular, rectangular cluster unit with two short Mo–Mo bonds, 2.211 (3) Å, and two long bonds, 2.901 (2) Å. The short Mo–Mo bonds are unsupported by bridging ligands but the long bonds are each bridged by two Cl atoms, and the coordination sphere of each Mo is completed by one Cl and one  $PEt_3$  terminal ligand. The Mo–Mo bond distances, diamagnetism, and number of electrons available for bonding are consistent with assessment of bonding in the rectangle as two triple and two single bonds, the tetrametal analogue of cyclobutadiyne.

Since the structural elucidation of the first compound characterized as having a metal–metal quadruple bond, and the subsequent proliferation of compounds having multiple bond order,<sup>1</sup> the potential reactivity of such compounds toward addition of molecular species across the multiple bond has been of considerable interest. However, until the present time few reactions of this type have actually been demonstrated.<sup>2</sup> We now report the preparation and structure of an unusually reactive quadruply bonded molybdenum dimer and the structural characterization of products resulting from its addition reactions.

It was our belief that reactivity of the quadruple bond could be promoted by preparing derivatives with weakly bonded ligands. Ligand dissociation in solution would then provide

species having lower coordination number and less hindered approach of substrate molecules to the region of the metal–metal bond. For this purpose our interest was drawn to the still unreported compound  $Mo_2Cl_4(PPh_3)_4$ . In our unsuccessful attempts to prepare this derivative we examined the reaction of  $(NH_4)_5Mo_2Cl_9 \cdot H_2O$  with triphenylphosphine in methanol, an approach known to be successful for preparation of other phosphine derivatives  $Mo_2Cl_4(PR_3)_4$ .<sup>3</sup> Instead, this reaction, even in the presence of a large excess of triphenylphosphine, has led to the new compound  $Mo_2Cl_4(PPh_3)_2(CH_3OH)_2$ .<sup>4</sup> Recrystallization of this product from methanol provided well-formed blue crystals of the solvate  $Mo_2Cl_4(PPh_3)_2 \cdot (CH_3OH)_2 \cdot nCH_3OH$ ,<sup>5</sup> which, however, dissociate and crumble upon removal of the solvent. Thus for the structure