the recovery of $(CH_3)_3SiC_6H_5$ (ca. 3 mmol; $\delta(CH_3)$ 0.08).

Cleavage of the tellurosilanes with selected protic species was similar to that observed[3a,4] for the selenosilanes; viz., $(CH_3)_3SiTeCH_3$ and $CH_3OH$ gave $(CH_3)_3SiOCH_3$ (95%), $(CH_3)_3SiTeCH_3$ and HBr gave $(CH_3)_3SiBr$ (91%), and $(CH_3)_3SiTeC_6H_5$ and $H_2O$ gave $[(CH_3)_3Si]_2O$ (92%). The tellurol byproducts were not estimated due to their ready decomposition to the corresponding ditellurides, hydrogen, and in some cases metallic tellurium. Benzenetellurol, $C_6H_5TeH$, was observed qualitatively in the NMR spectrum of the hydrolysis products of $(CH_3)_3SiTeC_6H_5$ [$\delta$(TeH) −2.4 ($J$(TeH) = 49.5 Hz)].

**(c) Reaction of Bromosilane with Lithium Organotellurolates.** Treatment of a diethyl ether slurry of crude $LiTeCH_3$ (ca. 0.4 g) with $H_3SiBr$ (ca. 1 mmol) at −78 °C gave $(H_3Si)_2Te$ (ca. 20%) and traces of silane as the only volatile silicon species. Similarly, no (organotelluro)silane was recovered from the reaction of $H_3SiBr$ and $LiTeC_6H_5$.

**Exchange Reactions of Trimethyl(organotelluro)silanes. (a) Reactions with Fluorogermanes.** In a typical experiment fluorogermane (1.60 mmol) and $(CH_3)_3SiTeCH_3$ (1.31 mmol) were allowed to react in an ampule (10 mL) at 25 °C (15 min). The products were fractionated by using baths at −23 and −196 °C. The former bath retained pure $H_3GeTeCH_3$ (1.22 mmol, 93%, *m/e* 212–224, $P^+ = [CH_6GeTe]^+$. Anal. Calcd for $CH_6GeTe$: Ge, 33.3. Found: Ge (as $GeH_3I$), 30.4.); the latter bath contained a mixture of $(CH_3)_3SiF$ (ca. 1.2 mmol) and unchanged $H_3GeF$ (ca. 0.35 mmol), identified by $^1H$ NMR spectra.[43] In similar experiments $H_3GeTeC_6H_5$ (91%), $(CH_3)_3GeTeCH_3$ (87%), and $(CH_3)_3GeTeC_6H_5$ (87%) were obtained from a deficit of the (organotelluro)silane with the corresponding fluorogermane. With use of $(CH_3)_2GeCl_2$ (1.18 mmol) with excess of $(CH_3)_3SiTeCH_3$ (3.09 mmol) the disubstituted species $(CH_3)_2Ge(TeCH_3)_2$ [1.05 mmol, 89%; $\delta(CH_3)$ 1.21, 1.67] was isolated as a nonvolatile orange oil. Raman lines assigned as skeletal modes were observed as follows ($cm^{-1}$): 599 (w, dp) and 567 (m, p), $\nu(GeC_2)$; 514 (s, p), $\nu$(CTe); 243 (m, dp) and 208 (vs, p), $\nu(GeTe_2)$; 192 (sh), 171 (vs, p), and 61 (vs, p), $\delta(GeTe_2)$. In a control experiment a 1:1 mixture of $(CH_3)_2GeCl_2$ and $(CH_3)_3SiTeCH_3$ gave only weak resonances at 1.21 and 1.67 ppm attributable to $(CH_3)_2Ge(TeCH_3)_2$ and strong additional lines at 1.30 and 1.74 ppm (integrated intensities 2:1) which we assign to the mixed chloro(methyltelluro) species $(CH_3)_2Ge(Cl)TeCH_3$. As found for other silicon- and germanium-group 6 compounds,[29,44] the value of $K_{25\,°C}$ of 1.6 for the equilibrium mixture is significantly less than the statistical random value of 0.25.

**(b) Reactions with Chlorostannanes.** Typically $(CH_3)_3SnCl$ (1.79 mmol) reacted smoothly with $(CH_3)_3SiTeCH_3$ (2.05 mmol) at 25 °C (15 min) to give $(CH_3)_3SnTeCH_3$ (1.69 mmol, 94%) as an involatile yellow oil. The volatile material contained only $(CH_3)_3SiCl$ and unchanged $(CH_3)_3SnCl$ as indicated by $^1H$ NMR spectra. Similarly $(CH_3)_3SnCl$ and $(CH_3)_3SiTeC_6H_5$ gave $(CH_3)_3SnTeC_6H_5$ (89%).

**(c) Reactions with Halosilanes.** Bromosilane (0.66 mmol) and a deficit of $(CH_3)_3SiTeCH_3$ (0.42 mmol) were sealed in a semimicro NMR tube. The NMR spectrum showed that no reaction had occurred after 5 min. After 15 min at 60 °C the NMR spectrum showed additional resonances in the ratio 1:1 at 3.8 and 1.6 ppm assigned to $H_3SiTeCH_3$ and a strong resonance at 0.57 ppm (intensity 3) assigned to $(CH_3)_3SiBr$, corresponding to ca. 10% reaction. After 10 h at 60 °C no $(CH_3)_3SiTeCH_3$ remained and the tube was reopened on the vacuum line and the products were fractionated by using traps held at −45 and −196 °C. The latter trap contained unchanged $H_3SiBr$ and $(CH_3)_3SiBr$ (molar ratio ca. 1:2) and the former trap (methyltelluro)silane, $H_3SiTeCH_3$ (0.38 mmol, 90%; *m/e* 170–176, $P^+ = [CH_nSiTe]^+$). A similar qualitative experiment using $H_3SiI$ and $(CH_3)_3SiTeCH_3$ showed complete exchange to $H_3SiTeCH_3$ and $(CH_3)_3SiI$ after 5 h at 60 °C. Cleavage of $H_3SiTeCH_3$ with HI gave $H_3SiI$ (87%). The exchange reaction between $(CH_3)_3SiTeC_6H_5$ and iodosilane led to the formation of $H_3SiTeC_6H_5$ (78%).

**Acknowledgment.** We thank the National Research Council of Canada for financial support.

**Registry No.** $H_3SiTeCH_3$, 34117-15-2; $H_2Si(TeCH_3)_2$, 73296-28-3; $H_3SiTeC_6H_5$, 73296-29-4; $H_2Si(TeC_6H_5)_2$, 73296-30-7; $(CH_3)_3SiTeCH_3$, 34117-12-9; $(CH_3)_3SiTeC_6H_5$, 73296-31-8; $H_3GeTeCH_3$, 34117-16-3; $H_3GeTeC_6H_5$, 73296-32-9; $(CH_3)_3GeTeCH_3$, 34117-13-0; $(CH_3)_3GeTeC_6H_5$, 73296-33-0; $(CH_3)_2Ge(TeCH_3)_2$, 73296-34-1; $(CH_3)_3SnTeCH_3$, 34117-14-1; $(CH_3)_3SnTeC_6H_5$, 73296-35-2; $(CH_3)_3PbTeCH_3$, 73296-36-3; $LiTeCH_3$, 60919-62-2; $LiTeC_6H_5$, 52251-60-2; $(CH_3)_3SiCl$, 75-77-4; $(CH_3)_3SiBr$, 2857-97-8; $[(CH_3)_3Si]_2O$, 107-46-0; $C_6H_5TeH$, 69577-06-6; $(CH_3)_3SiOCH_3$, 1825-61-2; $H_3SiBr$, 13465-73-1; $(H_3Si)_2Te$, 19415-73-7; $H_3GeF$, 13537-30-9; $(CH_3)_3GeF$, 661-37-0; $(CH_3)_2GeCl_2$, 1529-48-2; $(CH_3)_2Ge(Cl)TeCH_3$, 73296-37-4; $(CH_3)_3SnCl$, 1066-45-1; $H_3SiI$, 13598-42-0.

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# Binuclear Ferric Porphyrins Bridged by the Dianions of Hydroquinones

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*Received July 23, 1979*

Binuclear high-spin ferric porphyrin complexes containing hydroquinone dianion bridging moieties are formed by the reaction of $Fe^{II}$(TPP) (TPP is the dianion of *meso*-tetraphenylporphyrin) with several *p*-quinones including *p*-benzoquinone, tetrachloro-*p*-benzoquinone, tetrafluoro-*p*-benzoquinone, tetrabromo-*p*-benzoquinone, duroquinone, and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone. Two *o*-quinones, tetrachloro-*o*-benzoquinone and tetrabromo-*o*-benzoquinone, also react with $Fe^{II}$(TPP) to form binuclear ferric complexes with catechol dianion bridging moieties. In the case of the hydroquinone complexes, C–O IR stretching bands are identified in the range of 1431–1483 $cm^{-1}$ to support the presence of a dianionic hydroquinone bridging unit. $^{57}$Fe Mössbauer data indicate that the iron ions in both types of complexes are in the high-spin ferric state ($S = {}^5/_2$). The $[Fe(TPP)]_2$(hydroquinone) complexes exhibit weak antiferromagnetic exchange interactions ($\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$) with $J$ values ranging from −3.6 to −15.5 $cm^{-1}$. The tetrachlorocatecholate complex $[Fe(TPP)]_2(Cl_4cat)$ also exhibits a weak interaction with $J = -2.2$ $cm^{-1}$.

## Introduction

While it has been established that quinones play an integral role in electron-transport chains, interacting perhaps with iron metalloproteins,[2,3] only two studies dealing with the interaction of metalloporphyrins with quinones have appeared in the literature. Hill, Williams, and co-workers reported the results

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[1] A. P. Sloan Foundation Fellowship, 1976–1978.

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of a nuclear magnetic resonance study of porphyrin–quinone interactions in 1976.[4] Weak intermolecular complexes of cobalt(II) and nickel(II) mesoporphyrin dimethyl ester with 1,4-naphthoquinone, vitamin K-3, vitamin K-1, and ubiquinone were detected in solution. No quinone complexes were isolated, and no electron transfer from metal to quinone was observed. Castro and co-workers recently reported the results of a kinetics study of the oxidation and reduction of iron porphyrins and hemoproteins by quinones and hydroquinones.[5] No quinone complexes were isolated in this study, in which a variety of quinones were used to oxidize iron(II) porphyrin complexes.

Recently we demonstrated that the reaction of a *p*-quinone with 2 mol of Fe$^{II}$(salen) yields a binuclear complex with Fe$^{III}$(salen) units bridged by the dianion of a hydroquinone.[6] In this oxidative addition reaction the *p*-quinone experiences a two-electron reduction with the concurrent one-electron oxidation of each Fe$^{II}$(salen). Since Fe$^{II}$(TPP), where TPP is the dianion of *meso*-tetraphenylporphyrin, is a similar four-coordinate system which is readily oxidized by air in solution, the preparation of analogous hydroquinone dianion bridged ferric tetraphenylporphyrin dimers via this oxidative addition method was thought to be feasible. In this paper we wish to report the synthesis and characterization of a series of these ferric tetraphenylporphyrin complexes containing bridging units of reduced quinones.

## Experimental Section

**Physical Techniques.** Electronic absorption spectra were recorded on a Cary 14 spectrophotometer, and infrared spectra, obtained from samples prepared under argon as Nujol mulls, were run on a Perkin-Elmer Model 457 spectrophotometer.

Variable-temperature (4.2–286 K) magnetic susceptibility data were obtained with a Princeton Applied Research Model 150A vibrating sample magnetometer, which was operated at 13.5 kG. A calibrated GaAs temperature-sensitive diode was employed to monitor the temperature in conjunction with a CuSO$_2$·5H$_2$O standard. Least-squares computer fittings of the magnetic susceptibility data were accomplished with an adapted version of the function-minimization program known as STEPT.[7]

Iron-57 Mössbauer data, recorded at liquid-helium temperature, were obtained on an instrument previously described.[8] Liquid-nitrogen and room-temperature spectra were run on a second instrument.[9] Computer fitting of the $^{57}$Fe Mössbauer data to Lorentzian lines was carried out with a modified version of a previously reported program.[10]

Electron paramagnetic resonance (EPR) spectra were recorded on a Varian E-9 X-band spectrometer using an E101 microwave bridge with a 6 in. (10 kG) magnet. Measurements at 90 K were obtained by using a Dewar insert fabricated at the School of Chemical Sciences Glass Shop, University of Illinois. The magnetic field was calibrated with 2,2-diphenyl-1-picrylhydrazyl purchased from Aldrich.

All analytical data were obtained in the School of Chemical Sciences' Microanalytical Laboratory, University of Illinois.

**Compound Preparation.** All manipulations aimed at synthesizing quinone adducts of (*meso*-tetraphenylporphinato)iron(II), Fe$^{II}$(TPP), were performed under an atmosphere of purified argon in a Vacuum Atmospheres Corp. Dri-Lab equipped with an HE-493 Dri-Train. Argon was scrubbed of O$_2$ by MnO columns and then passed through 4A sieves to minimize the water content.[11]

Benzene and tetrahydrofuran (THF) were refluxed over and distilled from sodium/benzophenone under nitrogen. Bulk grade heptane was predried by chromatography over Alcoa F-20 alumina before being distilled from sodium/benzophenone under nitrogen. Absolute ethanol, used in the synthesis of Fe$^{II}$(TPP), was refluxed over magnesium ethoxide for 12 h and fractionally distilled under argon. All solvents were degreased in vacuo.

Reagent grade tetramethyl-*p*-benzoquinone (duroquinone, DuQ), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), tetrafluoro-*p*-benzoquinone (*p*-fluoranil, FQ), 2,6-di-*tert*-butyl-*p*-benzoquinone, (2,6-DBQ), tetrabromo-*o*-benzoquinone (*o*-bromanil), tetrachloro-*o*-benzoquinone (*o*-chloranil), and 3,5-di-*tert*-butyl-*o*-benzoquinone (3,5-DBQ) were used as purchased without further purification. Reagent grade *p*-benzoquinone (Q) was first sublimed and then recrystallized from tetrachloroethylene. Bianthrone (B) and tetrachloro-*p*-benzoquinone (ClQ) were recrystallized from THF and benzene, respectively. Practical grade 1,4-naphthoquinone (1,4-NQ) and tetrabromo-*p*-benzoquinone (*p*-bromanil, BrQ) were sublimed and then recrystallized from benzene. Technical grade 9,10-phenanthrenequinone was purified via the bisulfite addition product.[12] Recrystallization from toluene yielded pure yellow-orange needles. 1,2-Naphthoquinone was prepared from $\beta$-naphthol as described in the literature.[13]

**Fe$^{II}$(TPP).** *meso*-Tetraphenylporphyrin was prepared according to the method of Adler.[14] The preparations of (chloro)(*meso*-tetraphenylporphinato)iron(III), Fe(TPP)Cl,[15] and anhydrous bis(acetylacetonato)chromium(II), Cr(acac)$_2$,[16] were accomplished as described in the literature. Anhydrous FeCl$_2$, which was used in the preparation of Fe(TPP)Cl, was synthesized from sublimed anhydrous FeCl$_2$ following a literature method.[17] Fe$^{II}$(TPP) was synthesized in Schlenk apparatus in the drybox via the method of Collman,[18] by reacting Fe(TPP)Cl with anhydrous Cr(acac)$_2$ in an absolute ethanol/benzene mixture (1:10). The visible spectrum recorded for a benzene solution of this complex does not show any absorptions ascribable to Fe(TPP)Cl or [Fe(TPP)]$_2$O. In addition, the Nujol mull infrared spectrum verifies the complete absence of [Fe(TTP)]$_2$O. Excellent elemental analysis was obtained for the Fe$^{II}$(TPP).

**[Fe(TPP)]$_2$(DuQ)·THF.** Fe$^{II}$(TPP) (0.30 g, 0.45 mmol) was dissolved in THF (80 mL), filtered, and added to a solution of duroquinone (0.05 g, 0.31 mmol) in THF (20 mL). After the mixture was stirred for 7 days, the blue-purple microcrystalline product was filtered from the green-brown mixture, washed with THF (20 mL), and dried in vacuo 1 h. The yield was 0.29 g (82%).

Anal. Calcd for C$_{102}$H$_{76}$N$_8$Fe$_2$O$_3$: C, 77.86; H, 4.87; N, 7.12; Fe 7.10. Found: C, 77.78; H, 4.92; N, 7.03; Fe, 6.96.

**[Fe(TPP)]$_2$(ClQ)·THF and [Fe(TPP)]$_2$(BrQ)·2THF.** The binuclear ferric porphyrin complexes with bridging units consisting of the dianions of *p*-chloranil and *p*-bromanil were prepared in the same manner as above, with a reaction time of 24 h. The yields were similar to that obtained for [Fe(TPP)]$_2$(DuQ)·THF.

Anal. Calcd for [Fe(TPP)]$_2$(ClQ)·THF, C$_{98}$H$_{64}$N$_8$Cl$_4$Fe$_2$O$_3$: C, 71.12; H, 3.90; N, 6.77; Cl, 8.57; Fe, 6.75. Found: C, 71.34; H, 3.75; N, 6.45; Cl, 8.86; Fe, 6.61.

Anal. Calcd for [Fe(TPP)]$_2$(BrQ)·2THF, C$_{102}$H$_{72}$N$_8$Br$_4$Fe$_2$O$_4$: C, 64.31; H, 3.81; N, 5.88; Br, 16.78; Fe, 5.86. Found: C, 66.09; H, 3.67; N, 5.78; Br, 16.92; Fe, 5.92.

**[Fe(TPP)]$_2$Q·2THF.** Fe$^{II}$(TPP) (0.30 g, 0.45 mmol) was dissolved in THF (80 mL), filtered, and added to a solution of *p*-benzoquinone

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(0.03 g, 0.28 mmol) in THF (20 mL). A green-brown solution immediately formed. After the mixture was stirred for 48 h, heptane (50 mL) was added. The mixture was allowed to stand 1 h before being filtered. The blue-purple microcrystals were washed with a THF/heptane mixture (50:50, 20 mL) and dried in vacuo 1 h to yield 0.23 g (64%).

Anal. Calcd for $C_{102}H_{76}N_8Fe_2O_4$: C, 77.08; H, 4.82; N, 7.05; Fe, 7.03. Found: C, 77.39; H, 4.86; N, 6.89; Fe, 6.94.

**[Fe(TPP)]$_2$(FQ)·2THF and [Fe(TPP)]$_2$(DDQ)·2THF.** *p*-Fluoranil and DDQ were reacted with $Fe^{II}$(TPP) over a period of 24 h in the same manner as *p*-benzoquinone. The addition of heptane to the reaction mixture afforded yields similar to that obtained for the *p*-benzoquinone adduct.

Anal. Calcd for [Fe(TPP)]$_2$(FQ)·2THF, $C_{102}H_{72}N_8F_4Fe_2O_4$: C, 73.74; H, 4.37; N, 6.74; F, 4.57; Fe, 6.72. Found: C, 74.49; H, 4.35; N, 6.72; F, 4.82; Fe, 6.72.

Anal. Calcd for [Fe(TPP)]$_2$(DDQ)·2THF, $C_{104}H_{72}N_{10}Cl_2Fe_2O_4$: C, 73.12; H, 4.25; N, 8.20; Cl, 4.15; Fe, 6.54. Found: C, 73.08; H, 3.89; N, 8.17; Cl, 4.51; Fe, 6.65.

**[Fe(TPP)]$_2$(Cl$_4$cat).** $Fe^{II}$(TPP) (0.26 g, 0.39 mmol) and *o*-chloranil (0.10 g, 0.41 mmol) were stirred in benzene (15 mL) for 5 min. The green-brown reaction solution was filtered into heptane (100 mL), and the volume was concentrated to 75 mL by vacuum. Filtration afforded dark brown-purple microcrystals, which were washed with heptane (20 mL) and dried in vacuo 1 h. The yield was 0.23 g (75%).

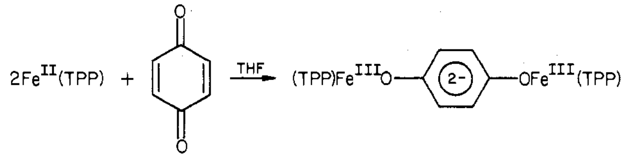
Anal. Calcd for $C_{94}H_{56}N_8Cl_4Fe_2O_2$: C, 71.32; H, 3.57; N, 7.08; Cl, 8.96; Fe, 7.06. Found: C, 71.77; H, 3.92; N, 6.98; Cl, 8.91; Fe, 6.71.

**[Fe(TPP)]$_2$(Br$_4$cat).** $Fe^{II}$(TPP) and *o*-bromanil were reacted in benzene and isolated by addition of heptane as detailed for [Fe(TPP)]$_2$(Cl$_4$cat).

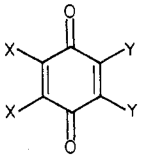
Anal. Calcd for $C_{94}H_{56}N_8Br_4Fe_2O_2$: C, 64.12; H, 3.21; N, 6.36; Br, 18.15; Fe, 6.34. Found: C, 64.89; H, 3.52; N, 6.36; Br, 19.42; Fe, 6.30.

## Results and Discussion

**Compound Formulation.** The reaction in THF of 1 mol of a *p*-benzoquinone with 2 mol of $Fe^{II}$(TPP) yields a binuclear complex comprised of two high-spin $Fe^{III}$(TPP) moieties bridged by a hydroquinone dianion.



The various *p*-benzoquinones that were found to react in this manner include



X = Y = H; Q
X = Y = Cl; ClQ
X = Y = Br; BrQ
X = Y = F; FQ
X = Y = $CH_3$; DuQ
X = Cl, Y = CN; DDQ

These binuclear ferric complexes are readily isolated as blue-purple crystalline solids. Exact stoichiometric ratios (2:1) of $Fe^{II}$(TPP) to *p*-benzoquinone need not be used, as addition of a large excess of *p*-benzoquinone still leads to formation of the binuclear complex. On the basis of elemental analytical data, the complexes of ClQ and DuQ are formulated as containing one THF solvate molecule while the others have two molecules of THF. All of these hydroquinone dianion bridged complexes are only slightly soluble in organic solvents. They appear to be relatively air stable once they are isolated and vacuum dried. Reactions involving the sterically hindered quinones, 2,6-di-*tert*-butyl-*p*-benzoquinone, 1,4-naphthoquinone, and bianthrone did not lead to the precipitation of 2:1 metal–quinone complexes.[19]

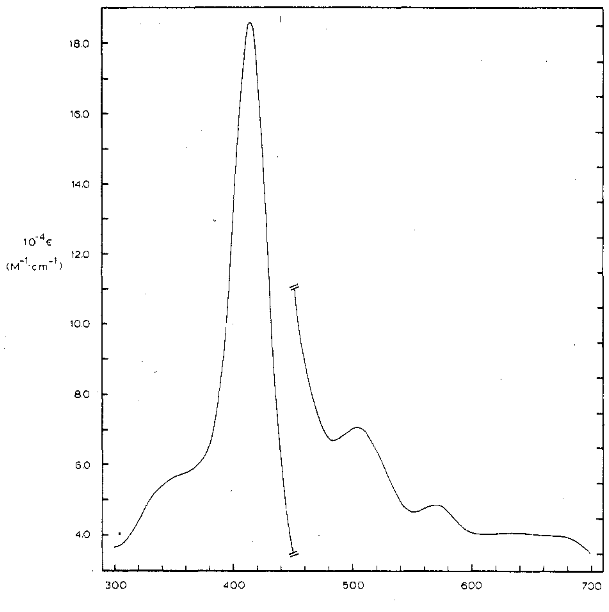


**Figure 1.** Electronic absorption spectrum for a benzene solution of [Fe(TPP)]$_2$(Cl$_4$cat).

The oxidative addition reaction of $Fe^{II}$(TPP) was also attempted with several *o*-quinones, including 9,10-phenanthrenequinone, 1,2-naphthoquinone, 3,5-di-*tert*-butyl-*o*-benzoquinone, *o*-chloranil, and *o*-bromanil. No semiquinone complexes were obtained with any of the *o*-quinones. In the case of *o*-chloranil and *o*-bromanil, 2:1 iron–quinone complexes were isolated, which physical data (vide infra) indicate to be comprised of high-spin $Fe^{III}$(TPP) moieties bridged in some manner by the dianion of the catechol. These two complexes are much more soluble in organic solvents than the hydroquinone complexes. They are remarkably soluble in benzene and can only be precipitated by addition of a large quantity of heptane and concentration of the resulting benzene/heptane solution. As with the hydroquinone complexes, these catechol complexes are air stable once dry. No appreciable decomposition was observed for [Fe(TPP)]$_2$(Cl$_4$cat) or [Fe(TPP)]$_2$(ClQ)·THF upon exposure to air over a 4-month period, as determined by elemental analytical data and infrared spectra.

**Electronic Absorption and Infrared Spectra.** The two catechol complexes appear green-brown in benzene solution with similar visible spectra. [Fe(TPP)]$_2$(Cl$_4$cat) exhibits five characteristic absorption bands in addition to a Soret band, as illustrated in Figure 1. In general, this spectrum is very similar to those of five-coordinate high-spin complexes such as Fe(TPP)Cl.[20] The spectrum for [Fe(TPP)]$_2$(Cl$_4$cat) has distinct, but subtle, differences from the spectra of six-coor-

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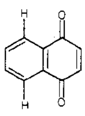
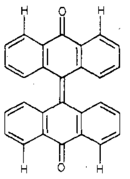
(19) The hydrogen atoms at $C_5$, $C_8$ in 1,4-naphthoquinone and at $C_1$, $C_8$, $C_1'$, $C_8'$ in bianthrone and the bulky tertiary butyl groups at $C_2$, $C_6$ in 2,6-DBQ evidently hinder the formation of binuclear complexes.



1,4-NQ



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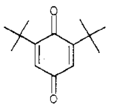

2,6-DBQ

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**Table I.** C–O Stretching Frequencies of *p*-Quinones, Semiquinones, and Dianions of Hydroquinones[a]

| quinone | $\nu_{CO}$ (quinone) | $\nu_{CO}$[d] (semiquinone) | $\nu_{CO}$[e] (coordinated hydroquinone dianion) |
|---|---|---|---|
| duroquinone | 1642[b] | | 1450 |
| *p*-benzoquinone | 1664[c] | | 1483 |
| *p*-bromanil | 1679[b] | 1515 | 1425 |
| *p*-chloranil | 1688[b] | 1538 | 1437 |
| *p*-fluoranil | 1694[b] | | 1482 |
| DDQ | 1667[d] | 1563 | 1431 |

[a] Obtained from samples prepared as Nujol mulls. [b] Kikot', B. S.; Matveeva, A. A.; Martynov, V. S.; Makarova, A. N.; Berlin, A. Ya. *J. Gen. Chem. USSR (Engl. Transl.)* 1968, *38*, 883. [c] Yates, P.; Ardao, M. I.; Fieser, L. F. *J. Am. Chem. Soc.* **1956**, *78*, 650. [d] Reference 23. [e] This work; obtained for Nujol mulls of [Fe(TPP)]$_2$(hydroquinone) complexes.

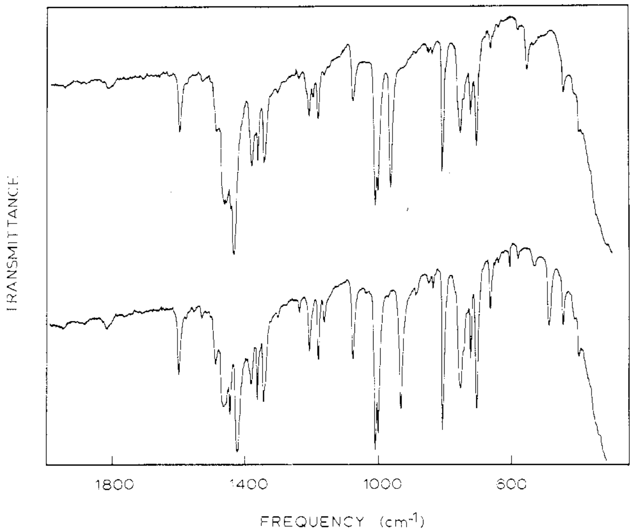

**Figure 2.** Nujol mull infrared spectra of [Fe(TPP)]$_2$(ClQ)·THF (top) and [Fe(TPP)]$_2$(BrQ)·2THF (bottom).

dinate, high-spin ferric porphyrins, such as bis(dimethyl sulfoxide)(tetraphenylporphinato)iron(III) perchlorate, [Fe(Me$_2$SO)$_2$(TPP)]ClO$_4$.[21] This suggests that the two catechol complexes have iron ions with five-coordinate square-pyramidal coordination geometries. It is significant to note that the UV–visible spectra of the two catechol-bridged ferric porphyrins differ greatly from the spectra of six-coordinate low-spin complexes such as bis(imidazole)(tetraphenylporphinato)iron(III) chloride, [Fe(TPP)(Im)$_2$]Cl,[22] and strongly exchange interacting binuclear ferric porphyrin complexes such as the $\mu$-oxo-bridged dimer [Fe(TPP)]$_2$O.[20]

The two-electron reduction of the quinone upon reaction with Fe$^{II}$(TPP) was monitored by infrared spectra, recorded from samples prepared as Nujol mulls under argon. As summarized in Table I, the free quinones have diagnostic C=O valence vibrations located in the 1630–1700-cm$^{-1}$ region. A one-electron reduction of the quinone to the semiquinone shifts this band approximately 150 cm$^{-1}$ to a lower wavenumber. A further one-electron reduction of the semiquinone to the dianion of the hydroquinone shifts the $\nu_{CO}$ to an even lower frequency.

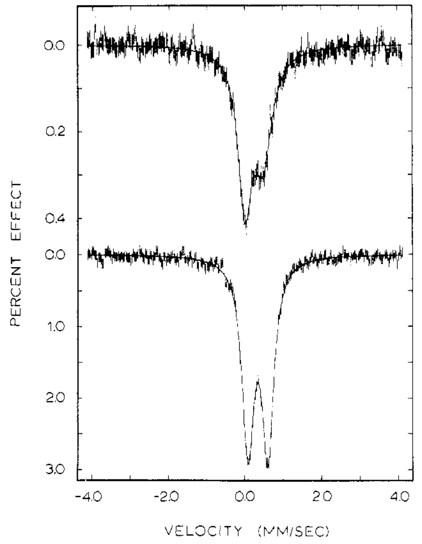

**Figure 3.** $^{57}$Fe Mössbauer spectra of [Fe(TPP)]$_2$(ClQ)·THF recorded at 295 K (top) and 4.2 K (bottom).

No C=O stretching band was observed for any of the complexes isolated in this study. As illustrated in Figure 2, the infrared spectra of [Fe(TPP)]$_2$(ClQ)·THF and [Fe(TPP)]$_2$(BrQ)·2THF do not have bands in the 1630–1700-cm$^{-1}$ region. However, strong bands are present at 1437 and 1425 cm$^{-1}$, respectively. These bands, which we attribute to the C–O stretch, are absent from the infrared spectrum of Fe$^{II}$(TPP). In Table I, it can be seen that the $\nu_{CO}$ bands for the semiquinones (as lithium salts) of *p*-bromanil and *p*-chloranil appear ca. 100 cm$^{-1}$ at higher frequencies than the $\nu_{CO}$ bands observed for these two porphyrin complexes. Thus, we conclude that the quinone moieties have been reduced to the hydroquinone dianions in [Fe(TPP)]$_2$(ClQ)·THF and [Fe(TPP)]$_2$(BrQ)·THF. Similar low-frequency $\nu_{CO}$ bands are readily detected for [Fe(TPP)]$_2$(FQ)·2THF and [Fe(TPP)]$_2$(DDQ)·2THF. The analogous bands for [Fe(TPP)]$_2$Q·2THF, [Fe(TPP)]$_2$(DuQ)·THF, [Fe(TPP)]$_2$(Cl$_4$cat), and [Fe(TPP)]$_2$(Br$_4$cat) are somewhat more difficult to discern. A strong absorption at 1483 cm$^{-1}$ may be reasonably assigned as the C–O stretch of [Fe(TPP)]$_2$Q·2THF. While this band appears to be superimposed upon a band ascribable to the porphyrin ligand, the intensity is much greater than that exhibited by Fe$^{II}$(TPP). The C–O stretching band for [Fe(TPP)]$_2$(DuQ)·THF is particularly difficult to identify. In an effort to determine if the C–O band for this compound is masked by the Nujol at 1450 cm$^{-1}$, the spectrum was also recorded as a fluorolube mull. A band at 1489 cm$^{-1}$ and a stronger band at 1450 cm$^{-1}$ are present in the fluorolube mull spectrum. We suggest that this latter absorption at 1450 cm$^{-1}$ is the C–O stretching band for this compound.

The infrared spectra attest to the complete absence of any [Fe(TPP)]$_2$O impurity. There is no evidence of the characteristic Fe–O–Fe bands, which occur at 875 (s) and 892 (m) cm$^{-1}$, seen for the $\mu$-oxo-bridged dimer.[20] The compound [Fe(TPP)]$_2$(DDQ)·2THF exhibits a sharp, medium intensity band at 2211 cm$^{-1}$, which is assignable as a C≡N stretching band of reduced DDQ. It has been noted before that this band is barely observable for free DDQ but is enhanced upon reduction to the semiquinone or hydroquinone.[23] The verification that the compounds contain THF solvate molecules is not possible with IR data. The strong THF band at ca. 1060 cm$^{-1}$ is masked by an even stronger band seen in this region for Fe$^{II}$(TPP). [Fe(TPP)]$_2$(Cl$_4$cat), which apparently does not contain THF, also shows a strong band in this region.

**$^{57}$Fe Mössbauer Spectroscopy.** Iron-57 Mössbauer data, which are summarized in Table II, clearly indicate that the complexes contain high-spin ferric ions. As seen in Figure 3,

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**Table II.** Iron-57 Mössbauer Parameters

| compd | temp, K | $\delta$,[a,b] mm/s | $\Delta E_Q$,[b] mm/s | $\Delta$,[b,c] mm/s | ref |
|---|---|---|---|---|---|
| $[Fe(TPP)]_2(DuQ)\cdot THF$ | 295 | 0.429 (6) | 0.389 (6) | 0.166 (6), 0.157 (6) | *d* |
| $[Fe(TPP)]_2Q\cdot THF$ | 295 | 0.346 (5) | 0.445 (5) | 0.220 (5), 0.221 (5) | *d* |
| $[Fe(TPP)]_2(BrQ)\cdot 2THF$ | 295 | 0.36 (1) | 0.45 (1) | 0.229 (8), 0.34 (1) | *d* |
| $[Fe(TPP)]_2(ClQ)\cdot THF$ | 295 | 0.474 (9) | 0.348 (9) | 0.216 (7), 0.30 (1) | *d* |
|  | 4.2 | 0.461 (3) | 0.521 (3) | 0.187 (3), 0.184 (3) | *d* |
| $[Fe(TPP)]_2(FQ)\cdot 2THF$ | 295 | 0.33 (1) | 0.47 (1) | 0.20 (1), 0.28 (1) | *d* |
| $[Fe(TPP)]_2(DDQ)\cdot 2THF$ | 295 | 0.354 (7) | 0.631 (7) | 0.198 (5), 0.306 (8) | *d* |
| $[Fe(TPP)]_2(Cl_4cat)$ | 295 | 0.329 (7) | 0.479 (7) | 0.182 (5), 0.237 (8) | *d* |
| $[Fe(TPP)]_2O$ | 300 | 0.29 | 0.62 |  | 26 |
| $[Fe(TPP)]_2N$ | 300 | 0.099 | 1.08 | 0.175 | 25 |
| $[Fe(salen)]_2Q$ | 295 | 0.359 (4) | 0.746 (4) | 0.208 (3), 0.300 (5) | 6 |
| $[Fe(salen)]_2(DuQ)\cdot THF$ | 100 | 0.497 (1) | 0.801 (2) | 0.202 (1), 0.252 (1) | 6 |

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

**Table III.** Magnetic Susceptibility Data and Parameters

|  | $\mu_{eff}$/Fe |  |  |  |  |
|---|---|---|---|---|---|
| compd | 286 K | 77 K | 4.2 K | $J$, cm$^{-1}$ | ref |
| $[Fe(TPP)]_2(DuQ)\cdot THF$ | 4.29 | 2.48 | 0.65 | −15.5 | *g* |
| $[Fe(TPP)]_2Q\cdot 2THF$ | 5.37 | 3.80 | 1.19 | −7.5 | *g* |
| $[Fe(TPP)]_2(BrQ)\cdot 2THF$ | 5.42 | 3.96 | 1.31 | −6.8 | *g* |
| $[Fe(TTP)]_2(ClQ)\cdot 2THF$ | 5.43 | 3.97 | 1.09 | −6.7 | *g* |
| $[Fe(TPP)]_2(FQ)\cdot THF$ | 5.42 | 4.74 | 1.51 | −3.8 | *g* |
| $[Fe(TPP)]_2(DDQ)\cdot 2THF$ | 5.78 | 4.81 | 1.43 | −3.6 | *g* |
| $[Fe(TPP)]_2(Cl_4cat)$ | 5.64 | 5.22 | 2.54 | −2.2 | *g* |
| $[Fe(salen)]_2(ClQ)$ | 5.61 | (5.21)[a] | (2.06)[b] | −2.0 | 6 |
| $[Fe(salen)]_2O$ | (1.85)[c] | (0.58)[d] |  | −95 | 33 |
| $[Fe(TPP)]_2O$ | (1.15)[e] | 0.45 |  |  | *h* |
|  | 1.74 |  |  |  | 26 |
|  |  |  |  | −155[f] | *i* |

[a] Actual measurements made at 86.1 K. [b] Actual measurements made at 5.2 K. [c] Actual measurements made at 287 K. [d] Actual measurements made at 82 K. [e] Actual measurements made at 293 K. [f] Obtained with nuclear magnetic resonance technique. [g] This work. [h] Fleisher, E. B.; Srivastava, T. S. *J. Am. Chem. Soc.* 1969, *91*, 2403. [i] Boyd, P. D. W.; Smith, T. D. *Inorg. Chem.* 1971, *10*, 2041.

$[Fe(TPP)]_2(ClQ)\cdot THF$ gives a spectrum consisting of an asymmetric quadrupole-split doublet at 295 K. The spectrum was least-squares fit to two Lorentzian line shapes, where the areas of the components of the doublet were held equal, to determine the isomer shift ($\delta$) and quadrupole splitting ($\Delta E_Q$) parameters. When the sample of $[Fe(TPP)]_2(ClQ)\cdot THF$ was cooled from 295 K to liquid-helium temperature, a spectrum was obtained which consists of a symmetric doublet with both component peaks having the same line widths. Similar asymmetric doublets are observed at room temperature for $[Fe(TPP)]_2(FQ)\cdot 2THF$, $[Fe(TPP)]_2(BrQ)\cdot 2THF$, $[Fe(TPP)]_2(DDQ)\cdot 2THF$, and $[Fe(TPP)]_2(Cl_4cat)$. Two of the compounds, $[Fe(TPP)]_2(DuQ)\cdot THF$ and $[Fe(TPP)]_2Q\cdot 2THF$, however, give symmetric doublets at room temperature. There is no evidence in any of the spectra of a signal due to the starting material $Fe^{II}(TPP)$.

The isomer shifts (vs. iron metal) observed for the compounds prepared in this work are well within the range (+0.25 to +0.60 mm/s) expected for iron(III) complexes, and the observed quadrupole splittings are diagnostic of the high-spin nature of each ferric ion.[24] In general, the observed quadrupole splittings (0.389–0.631 mm/s) are smaller than those reported for $[Fe(TPP)]_2N$ (1.08 mm/s)[21] and $[Fe(TPP)]_2O$ (0.62 mm/s).[25] Since several of the hydroquinone compounds are isolated with two THF solvate molecules, it is possible that the ferric ions are six-coordinate by virtue of the THF molecules binding in axial sites. The high-spin ferric complex $[Fe(Me_2SO)_2(TPP)]ClO_4$, however, has a much larger quadrupole splitting of 1.22 mm/s.[21] $[Fe(TPP)]_2(Cl_4cat)$ displays a quadrupole splitting value (+0.479 mm/s) that is very similar to the $p$-quinone adducts. This complex does not contain THF, and gives a visible absorption spectrum that is characteristic of five-coordinate high-spin ferric porphyrins.

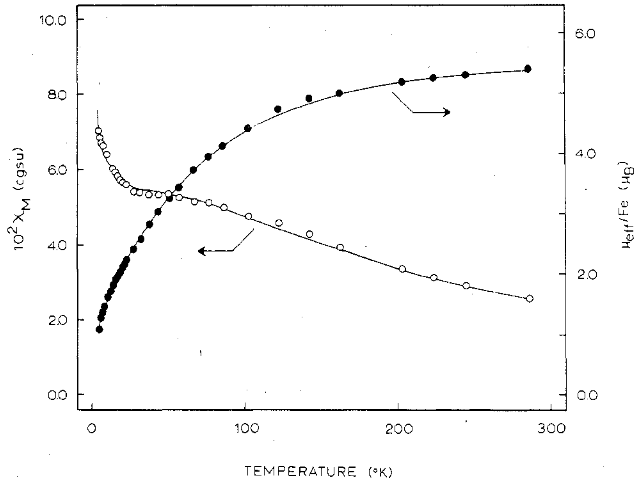

**Figure 4.** Molar paramagnetic susceptibility in cgsu and effective magnetic moment (per iron) in $\mu_B$ vs. temperature curves for $[Fe(TPP)]_2(ClQ)\cdot THF$. The solid lines result from least-squares fitting the data to the theoretical equation (see text).

It is of interest to note that the quadrupole splitting parameters associated with the $[Fe(TPP)]_2$(hydroquinone) complexes are ca. 0.5 mm/s less than those reported for the analogous salen complexes.[6,27] This is most likely a reflection of the ability of the salen ligand to fold back. The iron ion is less likely to be pulled out of the porphyrin plane and, consequently, the ferric ion chelated by the porphyrin ligand

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experiences less of an axial distortion.

**Magnetic Susceptibility.** Variable-temperature (4.2–286 K) magnetic susceptibility data are summarized in Table III. The magnetic susceptibility and effective magnetic moment ($\mu_{\text{eff}}$) vs. temperature curves for each compound are indicative of an antiferromagnetic exchange interaction. For example, $[\text{Fe(TPP)}]_2(\text{ClQ})\cdot\text{THF}$ has a $\mu_{\text{eff}}$/Fe value of 5.43 $\mu_B$ at 286 K, which gradually decreases to 3.97 $\mu_B$ at 77 K. Upon cooling of the complex to 4.2 K, $\mu_{\text{eff}}$/Fe falls off more rapidly to 1.09 $\mu_B$. Each complex apparently has a slight amount of a paramagnetic impurity. In the susceptibility vs. temperature curve given in Figure 4 for $[\text{Fe(TPP)}]_2(\text{ClQ})\cdot\text{THF}$, the small amount of paramagnetic impurity leads to an increase in $\chi_M$ with decreasing temperature below the Néel temperature. Such an impurity has been noted before for other antiferromagnetically coupled binuclear ferric porphyrins such as $[\text{Fe(TPP)}]_2\text{O}$[28] and $[\text{Fe(TPP)N}$.[25,29] X-Band EPR spectra measured for the compounds in this work verify the presence of this high-spin ferric impurity. The powder spectra taken at liquid-nitrogen temperature consist of signals at $g_\perp \approx 6$ and $g_\parallel \approx 2$, the characteristic features of tetragonally distorted high-spin ferric porphyrins.[30]

The theoretical $\chi_M$ expression for a binuclear $S_1 = S_2 = {}^5/_2$ complex involved in an isotropic magnetic exchange interaction ($\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$) and containing a paramagnetic impurity is given as[31]

$$\chi_M = \frac{2Ng^2\beta^2}{kT}\left(\frac{55 + 30z^{10} + 14z^{18} + 5z^{24} + z^{28}}{11 + 9z^{10} + 7z^{18} + 5z^{24} + 3z^{28} + z^{30}}\right) + \frac{4.2\chi_{\text{para}}}{T}$$

In this expression, the various symbols have their usual meanings, $z = \exp(-J/kT)$, and $\chi_{\text{para}}$ is the magnetic susceptibility of the paramagnetic impurity at 4.2 K. A least-squares fitting computer program was employed to fit the experimental data to this equation. As illustrated by the solid lines in Figure 4, an excellent fit to the data was obtained for $[\text{Fe(TPP)}]_2(\text{ClQ})\cdot\text{THF}$, where the exchange parameter, $J$, was found to be $-6.7$ cm$^{-1}$. The data for the other complexes were analyzed in the same manner to give the $J$ values listed in Table III. In each case, the amount of paramagnetic impurity as indicated by $\chi_{\text{para}}$ was found to be less than 5% by weight of the sample. The $g$ value was held constant at a value equal to or close to 2.0.

The antiferromagnetic exchange interactions propagated by the hydroquinone dianions are an order of magnitude weaker than that facilitated by the $\mu$-oxo bridge in $[\text{Fe(TPP)}]_2\text{O}$, where $J = -155$ cm$^{-1}$.[32] The interactions observed for the $[\text{Fe(TPP)}]_2$(hydroquinone) complexes are also greater than those seen for the analogous $[\text{Fe(salen)}]_2$(hydroquinone) complexes. For example, $[\text{Fe(salen)}]_2(\text{ClQ})$ ($J = -2.0$ cm$^{-1}$)[6] does not exhibit as strong an interaction as $[\text{Fe(TPP)}]_2(\text{ClQ})\cdot\text{THF}$ ($J = -6.7$ cm$^{-1}$). This trend is in keeping with the interaction trend seen for the $\mu$-oxo-bridged species, where $[\text{Fe(salen)}]_2\text{O}$ ($J = -95$ cm$^{-1}$)[33] exhibits a weaker interaction than $[\text{Fe(TPP)}]_2\text{O}$. Suggestions for this difference in interaction between the salen and the TPP species have been presented.[34]

**Table IV.** Oxidation-Reduction Potentials of Quinones[a]

| quinone | $E_0$, mV | ref |
|---|---|---|
| duroquinone | 463[b] | *e* |
| *p*-benzoquinone | 699,[b] 711[c] | *e, f* |
| *p*-bromanil | 746[c] | *f* |
| *p*-chloranil | 742[c] | *f* |
| *p*-fluoranil | | |
| DDQ | ca. 1000[c] | *g* |
| *o*-chloranil | 830[d] | *h* |
| *o*-bromanil | 814[d] | *h* |

[a] Conventional redox potential (at zero pH) for the reaction quinone + 2e$^-$ + 2H$^+$ $\rightleftarrows$ hydroquinone. For comparison, the redox potential for $\text{O}_2$ + 2e$^-$ + 2H$^+$ $\rightleftarrows$ $\text{H}_2\text{O}$ is +0.68 V; see: Latimer, W. M. "Oxidation Potentials", 2nd ed.; Prentice-Hall: Englewood Cliffs, N.J., 1952. [b] *p*-Benzoquinone (=699 mV) used as standard. [c] *p*-Benzoquinone (=711 mV) used as standard. [d] *o*-Benzoquinone (=795 mV) used as standard. [e] Musso, H.; Döpp, H. *Chem. Ber.* 1967, *100*, 3627. [f] Clark, W. M. "Oxidation Reduction Potentials of Organic Systems"; Williams and Wilkins: Baltimore, 1960. [g] Jackman, L. M. In "Advances in Organic Chemistry: Methods and Results"; Raphael, R. A., Taylor, E. C., Wynberg, H., Eds.; Interscience: New York, 1960; Vol. II, p 329. [h] Honer, L.; Geyer, E. *Chem. Ber.* 1965, *98*, 2016.

The $J$ values listed in Table III for the $[\text{Fe(TPP)}]_2$(hydroquinone) species where the bridge is derived from a *p*-quinone seem to parallel the oxidation potentials (see Table IV) of the various *p*-quinones. The durohydroquinone-bridged complex exhibits the weakest interaction. Thus, increasing the electron-withdrawing properties of the substituents on the benzene ring, as in the case of DDQ, decreases the interaction. Electron-donating groups on the benzene ring, then, increase the interaction. No such trend was noted for the $[\text{Fe(salen)}]_2$(hydroquinone) complexes.[6]

## Conclusions and Comments

Analytical and physical data indicate that the oxidative addition reaction between $\text{Fe}^{\text{II}}$(TPP) and a *p*-quinone yields a binuclear, high-spin ferric porphyrin where two $\text{Fe}^{\text{III}}$(TPP) moieties are bridged by a hydroquinone dianion. Sterically hindered *p*-quinones, such as 1,4-naphthoquinone, bianthrone, and 2,5-di-*tert*-butyl-*p*-benzoquinone, do not react with $\text{Fe}^{\text{II}}$(TPP) to form binuclear complexes. The inability of these three quinones to form such bridged complexes is a reflection of the coordination constraint placed on the iron by the tetraphenylporphinato ligand. The iron simply cannot be pulled significantly from the plane of the porphyrin. X-ray crystallographic data for five-coordinate iron(III) porphyrins have shown that the high-spin ferric ions cannot be displaced more than 0.50 Å from the porphinato plane.[35] The ferric irons are most likely in a five-coordinate, square-pyramidal coordination environment and are involved in an antiferromagnetic exchange interaction propagated by the hydroquinone dianion bridge.

High-potential *o*-quinones, *o*-chloranil and *o*-bromanil, react with $\text{Fe}^{\text{II}}$(TPP) to form 2:1 iron–catechol complexes, e.g., $[\text{Fe(TPP)}]_2(\text{Cl}_4\text{cat})$, which exhibit very weak antiferromagnetic exchange interactions. Even when 1:1 stoichiometric amounts of $\text{Fe}^{\text{II}}$(TPP) and *o*-chloranil are reacted, the bridged catechol system results, which is in keeping with our observations regarding the reaction of $\text{Fe}^{\text{II}}$(salen) with this *o*-quinone.[36] Electronic absorption spectra indicate that the ferric irons have five-coordinate square-pyramidal geometries. While the actual molecular structures of these apparently binuclear complexes are uncertain, it would seem reasonable to propose a bridged structure similar to the postulated structure of $[\text{Fe(salen)}]_2(\text{Cl}_4\text{cat})$, in which the catechol is

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coordinated via the oxygen atoms.[36]

At present, a number of iron complexes with quinone-like ligands are known. *o*-Semiquinone ligands are apparently stabilized when the *o*-semiquinone chelates to the iron(III) ion. Thus, the reaction of an *o*-quinone with $\mathrm{Fe(CO)_5}$ gives a complex which we have characterized as a tris(*o*-semiquinone) complex of high-spin iron(III).[37] The reaction of $\mathrm{Fe^{II}}$(salen) with an *o*-quinone gives an $\mathrm{Fe^{III}}$(salen)(*o*-semiquinone) complex,[36] in which the salen ligand folds back to allow chelation of the *o*-semiquinone ligand.

The preparation of a similar complex with a semiquinone ligand coordinated to an $\mathrm{Fe^{III}}$(TPP) moiety was not found to be possible. Repeated attempts to prepare such a complex by oxidative addition of $\mathrm{Fe^{II}}$(TPP) with 9,10-phenanthrenequinone, 1,2-naphthoquinone, and 3,5-di-*tert*-butyl-*o*-benzoquinone in several hydrocarbon solvents did not result in formation of an $\mathrm{Fe^{III}}$(TPP)(*o*-semiquinone) complex, because of the inability of the TPP ligand to fold back and permit chelation of the semiquinone to the iron. Finally, the reaction of a *p*-quinone with either $\mathrm{Fe^{II}}$(salen) or $\mathrm{Fe^{II}}$(TPP) does not yield a semiquinone complex, regardless of the stoichiometry of reactants. Two iron(II) complexes are oxidized with the concomitant two-electron reduction of the *p*-quinone to yield a binuclear ferric complex with a hydroquinone dianion as a bridge.

**Acknowledgment.** We are grateful for support from National Institutes of Health Grant HL 13652 and to Professor P. G. Debrunner and Mr. R. M. Emberson of the Department of Physics, University of Illinois, for their help in obtaining $^{57}$Fe Mössbauer data.

**Registry No.** $\mathrm{[Fe(TPP)]_2(DuQ)}$, 73367-26-7; $\mathrm{[Fe(TPP)]_2Q}$, 73367-27-8; $\mathrm{[Fe(TPP)]_2(BrQ)}$, 73367-28-9; $\mathrm{[Fe(TPP)]_2(ClQ)}$, 73367-29-0; $\mathrm{[Fe(TPP)]_2(FQ)}$, 73367-30-3; $\mathrm{[Fe(TPP)]_2(DDQ)}$, 73384-24-4; $\mathrm{[Fe(TPP)]_2(Cl_4cat)}$, 73367-31-4; $\mathrm{[Fe(TPP)]_2(Br_4cat)}$, 73367-32-5; $\mathrm{Fe^{II}TPP}$, 16591-56-3; DuQ, 527-17-3; Q, 106-51-4; BrQ, 488-48-2; ClQ, 118-75-2; FQ, 527-21-9; DDQ, 84-58-2; $\mathrm{Cl_4cat}$, 2435-53-2; $\mathrm{Br_4cat}$, 2435-54-3.

**Supplementary Material Available:** Tables V–XI (experimental and calculated magnetic susceptibility data for the compounds studied) (7 pages). Ordering information is given on any current masthead page.

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# Complexation of Lanthanides by Pyruvate

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*Received August 15, 1979*

Complexation of lanthanide cations by pyruvate was studied by titration calorimetry and $^1$H NMR. From the relative intensities of the NMR peaks and the net stability constants, estimates were obtained for the stability constants for formation of the lanthanide pyruvate species when the pyruvate is in the keto, diol, and dimer forms. Estimates are also reported for the enthalpies and entropies of complexation of these various species. Both the thermodynamic and $^1$H NMR data are consistent with binding of lanthanides only by carboxylate in the keto pyruvate complexes. However, in the diol complexes, chelation occurs via the $\alpha$-hydroxy and the carboxylate groups.

## Introduction

Complexation studies in aqueous solution of trivalent lanthanide ions with monocarboxylate and $\alpha$-substituted monocarboxylate ligands have been reported by a number of laboratories.[1] Of the $\alpha$-substituted ligands, amino and thio groups do not seem to be involved in the complexation while $\alpha$-hydroxy ligands form chelates.[2] A report of complexation of Eu(III) by pyruvate assumed interaction of the keto form of pyruvate although Leussing has reported that keto, diol (hydrated enol), and dimer species of pyruvate are involved in the complexation of Zn(II).[3]

In this paper we report our measurements of the thermodynamic parameters of complexation of Ln(III) ions and pyruvate by an entropy calorimetric titration procedure. We also report $^1$H NMR studies which provide information on the relative concentrations of the lanthanide complexes formed with the keto, diol, and dimer pyruvate species (Figure 1).

## Experimental Section

**Solutions for Calorimetry.** Stock solutions of the lanthanide perchlorates were prepared as described previously.[4] Working solutions of $\mathrm{Ln(ClO_4)_3}$ were prepared by diluting the stock solutions so that the final metal ion concentrations were approximately 0.025 M. The ionic strength of all the solutions was adjusted to 2.0 M with $\mathrm{NaClO_4}$, and the pH of the solutions was adjusted to a value between 2.0 and 2.2.

An aqueous stock solution of pyruvic acid was prepared from 25 g of reagent grade pyruvic acid (J.T. Baker Chemical Co.) and standardized against standard sodium hydroxide. The working solution of pyruvate was a buffer solution prepared by half neutralizing the pyruvic acid with an appropriate amount of sodium hydroxide. The ionic strength was maintained at 2.0 M by addition of $\mathrm{NaClO_4}$. The final solution was 0.50 M in pyruvic acid, 0.25 M in NaOH, and 1.75 M in $\mathrm{NaClO_4}$ at a pH of 2.2.

**Solutions for NMR.** Samples for NMR measurements were prepared by using solvent $\mathrm{D_2O}$ from Mallinckrodt Chemical Works with a minimum isotopic purity of 99.8%. The internal reference standard used in all samples was sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) from Merck Co.

The sodium pyruvate samples were prepared by dissolving a weighed amount of reagent grade sodium pyruvate in $\mathrm{D_2O}$. Solutions were adjusted to a pD range of 0–6.

Lanthanum and lutetium perchlorate solutions in $\mathrm{D_2O}$ were prepared by taking appropriate aliquots of the stock solutions to dryness several times in $\mathrm{D_2O}$. Sodium pyruvate was added to obtain a metal to ligand ratio of 6:1 at which most of the pyruvate is bound in the 1:1 complex. Lanthanum pyruvate solutions were prepared at pD 2 and 4 while lutetium pyruvate was prepared at pD 2 only due to its lower solubility at higher pD values.

**Calorimetry.** The calorimeter used in this study has been described in detail.[4] The general procedure used for calorimetric measurements in this study has been described by other workers from this laboratory.[4,5] The heats of complexation were obtained for all the lan-

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