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Novel Five-Coordinate Iron(III) Complexes Produced by Oxidation of Square-Planar (S = 1) Iron(II) Complexes

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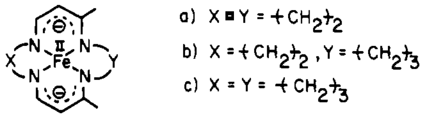
Received August 19, 1983

Reaction of macrocyclic square-planar tetraaza tetraenato(2–) iron(II) complexes **1** with a variety of oxidizing species has led to the isolation and characterization of a series of five-coordinate iron(III) complexes with dianionic 14-, 15-, and 16-membered macrocyclic ligands. The iron(III) complexes exist in the spin group states of $S = {}^1/_2, {}^3/_2$, or ${}^5/_2$, depending upon the axial ligand and size of the macrocyclic ligand. The unusual intermediate-spin $S = {}^3/_2$ ground state has been confirmed for many of these complexes by temperature-dependent susceptibility studies (2–350 K). Also included are the results of room-temperature Mössbauer spectral studies for all the new iron(III) derivatives.

Introduction

Earlier we reported the synthesis of a series of square-planar (S = 1) iron(II) complexes **1** prepared with 14-, 15-, and 16-membered macrocyclic ligands.[1,2] These square-planar iron(II) complexes **1** are very air sensitive and susceptible to oxidation under mild conditions. The oxidation chemistry of the three iron(II) complexes **1** was investigated with chemical reagents to determine the scope of their reactivity and to determine the effects of ring size on the oxidation reaction.



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In all cases the reactions reported here yield crystalline Fe(III) complexes, even though several attempts are discussed in which it was impossible to isolate pure products from the reaction. The oxidizing agents that were investigated included nitric oxide, dioxygen, halogen, halogenated hydrocarbons, and *p*-quinones. In all cases the products are obtained in high yield and are characterized as five-coordinate iron(III) complexes by elemental analyses, mass spectra, and solution molecular weight determinations. The spin state of the iron(III) has been found to depend not only on the axial donor but also significantly on the ring size of the in-plane macrocyclic ligand. For example, the only high-spin Fe(III) derivatives that were prepared contained either 15- or 16-membered rings. Conversely, there was no low-spin derivative isolated with the 16-membered ring. Metathesis reactions with the [I(tetraenatoN_4)Fe^{III}] complexes were carried out with a number of other ligands, producing complexes of the type [Fe(MAC^{2-})X], where X = Br^-, Cl^-, and NCS^-.

Finally, it is significant that most of these Fe(III) derivatives exist in the $S = {}^3/_2$ intermediate-spin ground state. Complexes known to exist in this intermediate-spin state include a five-coordinate [(pyridine)bis(dithiolene)iron(III)] complex,[3] the five-coordinate [Fe(Salen)CN] complex,[4] the five-coordinate [Fe(5-Cl-Salen)NO],[5] synthetic macrocyclic iron(III) complexes,[6] and a number of iron(III) porphyrin complexes.[7–9] In order to confirm the $S = {}^3/_2$ ground state for the new iron(III) complexes, extensive temperature-dependent magnetic susceptibility studies were performed. These results and the Mössbauer spectral results for all the new iron(III) complexes are discussed.

Experimental Section

Physical Measurements. ^{57}Fe Mössbauer spectra were obtained with a conventional constant-acceleration spectrometer operated in the time mode, with a ^{57}Co(Cu) source. Experiments were performed with both source and absorber at room temperature. The spectrometer was calibrated with a sodium nitroprusside standard; Fe_2O_3 and iron metal were employed as secondary standards. Isomer shifts and quadrupole splitting were determined by inspection with an accuracy of +0.01 mm/s. Samples of air-sensitive compounds were suitably encapsulated in an argon atmosphere by packing the compound into an aluminum die between two sheets of Mylar tape.

Visible and near-infrared spectra were obtained on a Cary Model 14-R recording spectrophotometer. Air-sensitive samples were all prepared in an inert atmosphere and placed in quartz cells tightly sealed with Teflon stoppers. For determination of extinction coefficients, stoppered volumetric flasks were weighed and then transferred to the glovebox, where an approximate weight of the compound was placed in the flask; the stoppered flask and contents were then removed from the glovebox, reweighed, and returned to the glovebox for solution preparation.

Infrared spectra were obtained with a Perkin-Elmer Model 337 recording spectrometer using Nujol mulls. Mulls of air-sensitive complexes were prepared in the glovebox, and their spectra were recorded immediately after removal from the glovebox.

Solid-state magnetic susceptibilities were measured by the Faraday method.[10] Diamagnetic corrections for ligands and counterions were made with use of Pascal's constants.[11] Measurements were made at room temperature under a pressure of 35 mm of helium gas. Variable-temperature (0–100 K) measurements of susceptibility were made by the use of a vibrating-sample magnetometer operating at a field strength of 10 kG and calibrated vs. nickel metal.[12] This method permits the facile measurement of the low-temperature susceptibility of air-sensitive compounds. The samples are packed into a preweighed Lucite holder in an inert-atmosphere drybox and then removed and reweighed. In addition variable-temperature susceptibilities were measured by the Faraday method in the temperature range 90–350 K. Solution susceptibilities were measured

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0020-1669/84/1323-3235$01.50/0

Table I. Analytical Data for the New Iron(III) Complexes

	% C		% H		% N		% halide	
compd	calcd	found	calcd	found	calcd	found	calcd	found
[Fe(Me$_2$[14]tetraenatoN$_4$)Cl]	46.55	46.85	5.86	5.72	18.10	18.01	11.45	10.95
[Fe(Me$_2$[14]tetraenatoN$_4$)Br]	40.71	40.60	5.09	5.06	15.83	15.77	22.55	22.65
[Fe(Me$_2$[14]tetraenatoN$_4$)I]	35.94	35.89	4.52	4.59	13.97	13.81	31.64	31.49
[Fe(Me$_2$[14]tetraenatoN$_4$)(NO)]	47.40	47.69	5.92	5.89	23.04	23.47		
[Fe(Me$_2$[14]tetraenatoN$_4$)(NCS)]	47.02	46.87	5.42	5.24	21.09	21.34		
[Fe(Me$_2$[14]tetraenatoN$_4$)$_2$Q]	54.81	54.69	6.09	6.34	17.07	16.93		
[[Fe(Me$_2$[14]tetraenatoN$_4$)]$_2$QCl]	45.37	45.57	4.57	4.50	14.11	14.01	17.86	17.83
[Fe(Me$_2$[15]tetraenatoN$_4$)Cl]	48.25	47.91	6.23	6.03	17.31	17.41	10.95	10.84
[Fe(Me$_2$[15]tetraenatoN$_4$)Br]	42.42	42.19	5.48	5.51	15.22	15.11	21.71	21.63
[Fe(Me$_2$[15]tetraenatoN$_4$)I]	37.59	37.41	4.82	5.00	13.49	12.95	30.60	30.37
[Fe(Me$_2$[15]tetraenatoN$_4$)(NO)]	49.72	49.23	6.29	6.42	22.03	21.97		
[Fe(Me$_2$[15]tetraenatoN$_4$)(NCS)]	48.56	48.55	5.82	5.51	20.23	19.99		
[[Fe(Me$_2$[15]tetraenatoN$_4$)]$_2$Q]	56.15	56.24	6.48	6.60	16.37	16.64		
[[Fe(Me$_2$[15]tetraenatoN$_4$)]$_2$QCl]	46.75	46.38	4.91	4.95	13.63	13.56	17.25	17.70
[Fe(Me$_2$[16]tetraenatoN$_4$)Cl]	49.80	50.04	6.57	7.12	16.59	16.19	10.50	10.90
[Fe(Me$_2$[16]tetraenatoN$_4$)I]	39.19	39.04	5.13	5.23	13.06	12.76	29.60	29.37
[[Fe(Me$_2$[16]tetraenatoN$_4$)]$_2$Q]	57.31	57.49	6.79	6.81	15.73	15.52		
[[Fe(Me$_2$[16]tetraenatoN$_4$)]$_2$QCl]	48.01	48.28	5.26	5.40	13.17	13.25	16.67	16.72

by the Evans method[13] on a Varian A-60 NMR spectrometer using $CHCl_3$ as the solvent.

Conductance measurements were made with an Industrial Instruments Model RC 16B conductivity bridge. The conductance measurements were made at 25 °C at 1000 Hz on 10^{-3} M solutions in the drybox. Analyses were performed by Galbraith Laboratories. Mass spectra were obtained with an MS-9 spectrometer at an ionizing potential of 70 eV. Molecular weights were obtained on a Mechrolab Osmometer Model 301A using chloroform solutions.

Materials. Diethyl ether and ethanol were distilled from calcium hydride, and chloroform and benzene were stored over molecular sieves and distilled before use. All salts, LiCl, LiBr, and NaSCN, were dried at 100 °C for 48 h prior to their use. All distillations were carried out under a nitrogen atmosphere, and all syntheses and manipulations of iron complexes were carried out under nitrogen.

Syntheses. [Fe(Me$_2$[14]tetraenatoN$_4$)I]. To 1.0 g (3.65 mmol) of [Fe(Me$_2$[14]tetraenatoN$_4$)](**1a**) dissolved in 50 mL of warm benzene is added 0.46 g (1.88 mmol) of I_2 dissolved in benzene. An immediate reaction takes place as evidenced by the color change to a deep red. When the solution is cooled, crystals form and are collected by filtration. They are recrystallized from a 1:1 mixture of chloroform–benzene, washed with diethyl ether, and dried in vacuo. Final yield was always in the range 70–80% based on the starting complex; in a typical preparation 1.1 g of product was obtained.

[Fe(Me$_2$[14]tetraenatoN$_4$)X] (Where X = Cl, Br, or NCS). One gram of the iron(III) complex [Fe(Me$_2$[14]tetraenatoN$_4$)I] is stirred in 50 mL of hot absolute ethanol, and to this is added an ethanolic solution containing 1.0 g of the appropriate dry salt, i.e., LiCl, LiBr, or NaNCS. In each case the solutions are allowed to cool to room temperature after 1 h and then stirred for an additional 24 h. The products crystallize from the absolute ethanol and are collected via filtration. The crude products are then recrystallized from chloroform and diethyl ether. Yields for the thiocyanate derivative were consistently higher, 60–80%, than for the others due to its lower solubility in ethanol. In typical preparations the yields were 0.52 g of the thiocyanate derivative, 0.38 g of the bromide derivative, and 0.30 g of the chloride complex.

[Fe(Me$_2$[14]tetraenatoN$_4$)NO]. Nitric oxide gas, NO, is bubbled through a benzene solution containing 1.0 g of [Fe(Me$_2$[14]tetraenatoN$_4$)]. An immediate reaction occurs and is accompanied by the formation of black-brown crystals. After exposure to nitric oxide for 1 h, the volume of benzene is reduced to 10 mL and a crystalline product is collected by filtration, washed with diethyl ether, and then dried in vacuo. The yield was 0.80 g (72%).

[[Fe(Me$_2$[14]tetraenatoN$_4$)]$_2$Q]. To a benzene solution containing 1.0 g (3.65 mmol) of compound **1a** is added a benzene solution containing 0.2 g (1.88 mmol) of *p*-benzoquinone. An immediate reaction takes place, and as the solution cools, a precipitate forms. The red-brown solid is collected by filtration and recrystallized from chloroform and diethyl ether. The yield was 0.90 g (75%) of the quinone-bridged dimer.

[[Fe(Me$_2$[14]tetraenatoN$_4$)]$_2$QCl]. The same procedure was used to prepare this complex as was used in the preceding preparation, but *p*-tetrachlorobenzoquinone was used in place of *p*-benzoquinone. The yield was 80% based on starting iron(II) complex **1a**.

[Fe(Me$_2$[15]tetraenatoN$_4$)I]. This complex was prepared by the same method as used for the preparation of the 14-membered derivative [Fe(Me$_2$[14]tetraenatoN$_4$)I]. The yields of the desired product based on starting complex **1b** were in the range 65–75%.

[Fe(Me$_2$[15]tetraenatoN$_4$)X] (Where X = Cl, Br, or NCS). These three complexes were prepared by the same route outlined above for the 14-membered complexes. The yields were less due to a higher solubility of the complexes. Yields were obtained in the range 30–40% for the chloride and bromide complexes and 50% for the thiocyanate complex.

[Fe(Me$_2$[15]tetraenatoN$_4$)NO]. This complex was prepared by the same method outlined for the 14-membered nitrosyl adduct, except that diethyl ether was used as the solvent in place of benzene. The yield based on complex **1b** was 85%.

[[Fe(Me$_2$[15]tetraenatoN$_4$)]$_2$Q] and [[Fe(Me$_2$[15]tetraenatoN$_4$)]$_2$QCl]. These two dimeric complexes were prepared by the same method used for the 14-membered quinone dimers, except that the solvent was diethyl ether. The yields for both dimeric complexes were in the range 80–85% based on complex **1b**.

[Fe(Me$_2$[16]tetraenatoN$_4$)I]. To a benzene solution containing 2.0 g (6.62 mmol) of [Fe(Me$_2$[16]tetraenatoN$_4$)] (**1c**) was added a benzene solution containing 0.84 g (3.31 mmol) of I_2. An immediate reaction takes place to form a green solution. The solvent is removed by vacuum until the volume reaches 20 mL; at this point the dark green crystals that have formed are collected by filtration. The product is recrystallized from hot 4:1 benzene–THF solvent mixture. The final yield based on starting complex **1c** is 55% (1.56 g).

[Fe(Me$_2$[16]tetraenatoN$_4$)Cl]. This complex is prepared by metathesis of the iodide complex with excess LiCl in hot ethanol, as described for the 14-membered complexes. The volume of the solution is reduced to 5 mL and allowed to stand 16 h. Crystals form but are impure due to cocrystallization of salts. The crude product was recrystallized from chloroform–diethyl ether. The yield based upon 1.5 g of starting iodide complex was 0.28 g (25%).

[[Fe(Me$_2$[16]tetraenatoN$_4$)]$_2$Q] and [[Fe(Me$_2$[16]tetraenatoN$_4$)]$_2$QCl]. These two dimeric complexes were prepared by the same methods outlined above for the 15-membered quinone dimers using diethyl ether as the solvent. After recrystallization from chloroform, the yields were between 70 and 80% based on the starting iron(II) complex **1c**.

Results and Discussion

Syntheses. All of the new five-coordinate iron(III) complexes reported here have been characterized by elemental analyses (Table I) and mass spectra, when possible. In all cases the formulation of the complexes as five-coordinate iron(III) derivatives is in agreement with the results of these measurements. Solutions of all of these complexes are both oxygen and water sensitive. The presence of water causes the immediate formation of brown insoluble products, and expo-

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Table II. Physical Properties of the Iron(III) Complexes

compd	color	μ_{eff}, μ_B	mol wt		
			MS, m/e		osmometry[b]
			calcd	found	found
[Fe(Me_2[14]tetraenatoN_4)I]	red	3.94	401	401	
[Fe(Me_2[14]tetraenatoN_4)Br]	red-brown	3.98	354	354	
[Fe(Me_2[14]tetraenatoN_4)(Cl)]	red-brown	3.93, 3.8[c]	309	309	311
[Fe(Me_2[14]tetraenatoN_4)NO]	red-brown	1.95	304	304	
[Fe(Me_2[14]tetraenatoN_4)NCS]	red-brown	3.91	331	331	
[[Fe(Me_2[14]tetraenatoN_4)]$_2$Q]	red-brown	3.73	...	...	
[[Fe(Me_2[14]tetraenatoN_4)]$_2$QCl]	red-brown	3.85	794	...	770
[Fe(Me_2[15]tetraenatoN_4)I]	red-brown	4.14	415	415	
[Fe(Me_2[15]tetraenatoN_4)Br]	red-brown	3.90	367	367	
[Fe(Me_2[15]tetraenatoN_4)Cl]	red-brown	3.77, 3.9[c]	323	323	328
[Fe(Me_2[15]tetraenatoN_4)NO]	red-brown	1.98	318	318	
[Fe(Me_2[15]tetraenatoN_4)NCS]	red-brown	4.05, 3.70[d]	346	346	
[[Fe(Me_2[15]tetraenatoN_4)]$_2$Q]	red-purple	5.60	684	...	
[[Fe(Me_2[15]tetraenatoN_4)]$_2$QCl]	red	4.14	822	...	803
[Fe(Me_2[16]tetraenatoN_4)I]	green	4.36	429	429	
[Fe(Me_2[16]tetraenatoN_4)Cl]	red-brown	3.98, 4.2[c]	337	337	351
[[Fe(Me_2[16]tetraenatoN_4)]$_2$Q]	purple	5.61	712	...	
[[Fe(Me_2[16]tetraenatoN_4)]$_2$QCl]	purple	5.60	850	...	891

[a] Magnetic moments at 25 °C. [b] Solution molecular weights in $CHCl_3$. [c] Magnetic moment in $CHCl_3$ solution by Evans' method. [d] Solid-state magnetic moment at 107 K.

sure to dry oxygen yields intractable precipitates. For these reasons the syntheses and manipulations of solutions of these materials were performed under a dry nitrogen atmosphere. The solid materials are not air sensitive for periods of up to several days.

The reactions of the square-planar iron(II) $S = 1$ complexes (**1a–c**) with the oxidizing agents iodine, *p*-tetrachlorobenzoquinone, and *p*-benzoquinone proceed readily and give crystalline products in high yields. The five-coordinate iodo complexes undergo metathesis reactions to yield the thiocyanate, chloro, and bromo derivatives. Metathesis from the 16-membered ring iron(III)–iodo complex yielded only the chloro derivative. This is believed to result from the trend in the increased solubility of the iron(III) complex with increasing ring size.

The reaction of iron(II) complexes **1** with nitric oxide, NO, gas provides another example of a ring-size effect. The reaction proceeds smoothly for both the 14- and 15-membered ring complexes **1a** and **1b** but yields only an intractable brownish precipitate when the 16-membered complex **1c** is used.

In addition to these reactions, the square-planar iron(II) complexes **1** were caused to react with chlorine, bromine, and oxygen. All attempts with these oxidants (even at low temperatures, −60 °C) gave only intractable brown precipitates. Apparently, the more potent oxidizing agents attack the ligands, as well as the iron(II) center. As a result, intractable degradation products result.

Attempts to prepare the oxo-bridged iron(III) dimers via metathesis reactions with the previously prepared iron(III) iodide complexes were unsuccessful. All of the iron(III) complexes were treated with the following reagents: Ag_2O in ethanol and 2 equiv of dry KOH in ethanol.[14] Although a reaction took place in each case, pure products could not be isolated since they were extremely soluble: only impure red-brown powders were isolated.

The reaction with halogenated hydrocarbons also result in the oxidation of the square-planar complexes **1**. For example, benzene solutions of the iron(II) complexes react with such halogenated hydrocarbons as $CHCl_3$ and benzyl halides but not with primary alkyl halides.[15] The reaction with benzyl halides is slow and requires about 2 weeks for completion; whereas that with $CHCl_3$ is much faster, requiring several hours. In these reactions there is a very fast initial reaction, followed by the slow production of the iron(III) halide complex and the coupled organic product. The products have not been isolated but have been identified by comparison of their electronic spectra to those of authentic materials. White crystals of 1,2-diphenylethane were isolated from the reaction of benzyl iodide with [Fe(Me_2[14]tetraenatoN_4)] (**1a**) and identified by its mass spectrum (*m/e*: calcd, 182; found, 182) and its melting point (found, (mp 49–50°C; lit.[16] mp 52 °C). These results and observations are consistent with a free radical oxidation mechanism consisting of two steps: (1) the first step is fast and produces a mixture of Fe(III) halide and Fe(III) alkyl derivatives; (2) the second step involves the slow homolytic dissociation of the Fe(III) alkyl (perhaps catalyzed by light[17,18]), followed by reaction with more alkyl halide to give Fe(III) halide and the coupled organic product. Such reactions are reminiscent of the oxidation of Co(II) chelates[19] and iron(II) porphyrins[20] by organic halides.

Characterization of the Iron(III) Complexes. Support for the five-coordinate formulation for the structures of these iron(III) derivatives is based initially on their elemental analyses and mass spectra (Tables I and II), but additional confirmation comes from solution molecular weight determinations on a few selected compounds (Table II). The determination of the molecular weight by osmometry was complicated by the air sensitivity of these complexes. As a result, only the less reactive complexes were studied. The results for the iron(III) chloro complexes establishes the monomeric structure for these derivatives in solution and supports the results of mass spectral measurements. Since the *p*-quinone oxidation products decompose in the mass spectrometer, it was especially important to confirm their dimeric formulation by a solution molecular weight determination. The *p*-benzoquinone products are too air sensitive in solution to permit this measurement, but the *p*-tetrachlorobenzoquinone complexes are stable enough to permit the measurement of their solution

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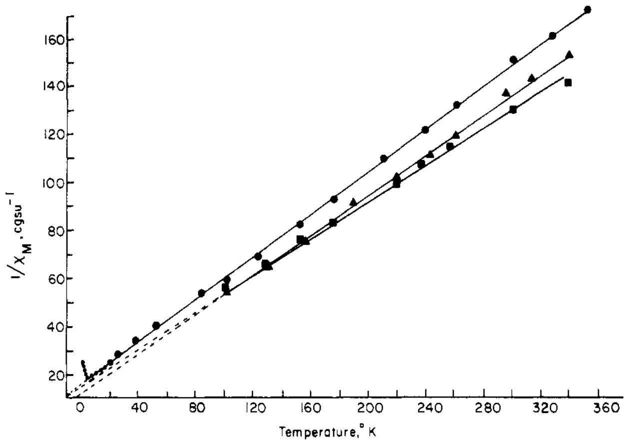

Figure 1. Graph of $1/\chi_M$ vs. temperature for (●) [Fe(Me$_2$[14]tetraenatoN$_4$)I], (▲) [Fe(Me$_2$[15]tetraenatoN$_4$)I], and (■) [Fe(Me$_2$[16]tetraenatoN$_4$)I].

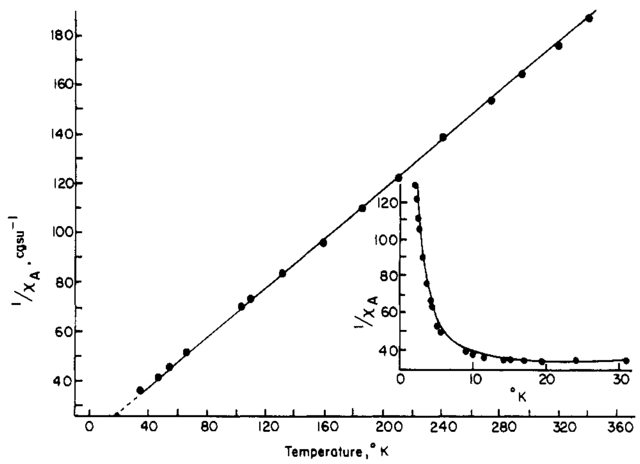

Figure 2. Graph of $1/\chi_A$ vs. temperature for [[Fe(Me$_2$[14]tetraenatoN$_4$)]$_2$QCl].

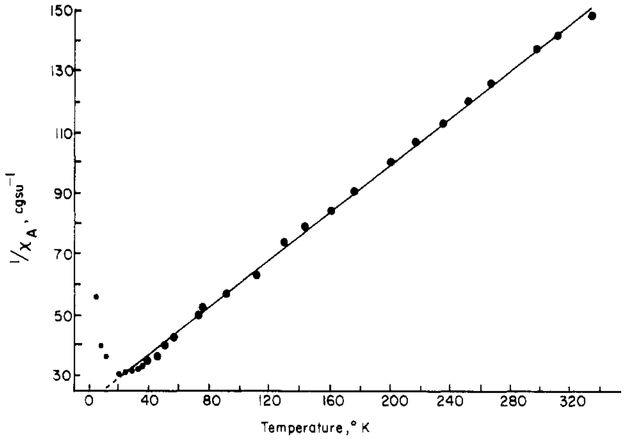

Figure 3. Graph of $1/\chi_A$ vs. temperature for [[Fe(Me$_2$[15]tetraenatoN$_4$)]$_2$QCl].

molecular weights. The results for the three derivatives prepared by oxidation with *p*-tetrachlorobenzoquinone definitely confirm their dimeric formulation (Table II).

The infrared spectra of these iron(III) complexes have been important in their characterization. For all of the iron(III) derivatives the absorption pattern of the double-bond region is virtually the same as that found in the starting iron(II) complexes **1**. This indicates that the ligands have not been transformed and that during the course of these oxidation reactions the oxidations are confined to the metal center. There is a broad and intense band observed in the infrared spectra of each nitrosyl adduct (ν(NO) = 1580 cm^{-1} in CHCl$_3$). This low value for the NO stretching mode[21] is consistent with the presence of iron(III) and a negatively charged NO$^-$ ligand, although formal oxidation-state assignments are tenuous[22] since this system is best described by a molecular orbital model. The IR absorption pattern observed for the thiocyanate absorptions ν(CN) = 2050 cm^{-1} and ν(CS) = 770 cm^{-1} in the two thiocyanato complexes is consistent with N-bonded thiocyanate.[23]

Magnetic Susceptibility Studies. The room-temperature magnetic moments of all the new iron(III) complexes are listed in Table II. From the room-temperature data the low-spin ($S = {}^1/_2$) ground state has been assigned to the 14- and 15-membered ring nitrosyl adducts. Three of the dimeric complexes produced via oxidation with *p*-quinones have high magnetic moments (5.6 μ_B) that are somewhat smaller than is expected for high-spin ($S = {}^5/_2$) iron(III) (spin-only μ_{eff} = 5.92 μ_B). The remaining 13 complexes all display anomalous moments in the range 3.73–4.36 μ_B. For the three iron(III) chloro derivatives, the solution moments[13] were found to be the same as the values observed in the solid state ($\sim$3.9 μ_B). Thus, it is assumed that the source of the intermediate susceptibility values is not due to solid-state effects for any of these complexes.

In order to determine the nature of the ground spin states (either $S = {}^3/_2$ or a thermal equilibrium between $S = {}^1/_2$ and $S = {}^5/_2$), the temperature-dependent magnetic susceptibilities were determined for a number of these complexes. In Figure 1 the graph of $1/\chi_M$ vs temperature for the three iodide complexes is shown. For the 15- and 16-membered ring iodide complexes, this plot is linear above 100 K, and for the complex [Fe(Me$_2$[14]tetraenatoN$_4$)I], the graph is linear above 9 K. From the Curie–Weiss law expression $1/\chi_M = C/(T + \Theta)$, the magnetic moments and Weiss constants were calculated: [Fe(Me$_2$[14]tetraenatoN$_4$)I], μ_{eff} = 4.22 μ_B and Θ = 15 K; [Fe(Me$_2$[15]tetraenatoN$_4$)I], μ_{eff} = 4.12 μ_B and Θ = 6 K; [Fe(Me$_2$[16]tetraenatoN$_4$)I], μ_{eff} = 4.20 μ_B and Θ = 12.8 K. These results confirm that the ground spin state is the $S = {}^3/_2$ intermediate-spin state for these five-coordinate iron(III) complexes. Another independent check of this assignment was made by measuring the magnetic moment of [Fe(Me$_2$[15]tetraenatoN$_4$)NCS] at 107 K, where μ_{eff} was found to be 3.70 μ_B. Thus, it is assumed that all of the remaining five-coordinate monomeric iron(III) complexes have the $S = {}^3/_2$ ground spin state. It also is interesting to note that the complex [Fe(Me$_2$[14]tetraenatoN$_4$)I] displays antiferromagnetic behavior at very low temperature; i.e., T_n = 5 K.

The remaining six *p*-quinonate(2–)-bridged dimers required independent confirmation of their ground states, since unusual magnetic moments can arise[15,25,26] from spin–spin coupling between iron(III) centers in dimers. In Figures 2 and 3 are shown the plots of $1/\chi_A$ vs. temperature over the range 1–350 K for the *p*-tetrachloroquinonate(2–)-bridged dimers of the 14- and 15-membered ring complexes. The 14- and 15-membered ring dimeric complexes obey the Curie–Weiss law ($1/\chi_M = C/(T + \Theta)$) at temperatures greater than 30 K and give the following values: [[Fe(Me$_2$[14]tetraenatoN$_4$)]$_2$QCl], μ_{eff} = 4.02 μ_B and Θ = 37 K; [[Fe(Me$_2$[15]tetraena-

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Table III. Electronic Spectra of the Iron(III) Complexes

compd	abs bands[a]
$[Fe(Me_2[14]tetraenatoN_4)Cl]$	7.41 (20.6), 10.0 (sh), 12.05 (275), 15.9 (sh), 19.23 (2400), 21.9 (2335), 26.0 (sh), 30.9 (7200)
$[Fe(Me_2[14]tetraenatoN_4)Br]$	7.25 (35), 10.2 (41), 19.23 (4141), 21.76 (3272), 31.75 (3330)
$[Fe(Me_2[14]tetraenatoN_4)I]$	7.7 (40), 11.6 (80), 18.52 (4500), 21.3 (4600), 32.0 (7540)
$[Fe(Me_2[14]tetraenatoN_4)NO]$	10.6 (sh, ~160), 13.5 (sh), 23.8 (3210), 27.0 (7060), 34.2 (18 000)
$[Fe(Me_2[14]tetraenatoN_4)NCS]$	7.3 (205), 11.8 (sh, ~230), 15.87 (sh, ~871), 19.76 (3255), 24.0 (4052), 31.25 (8710)
$[[Fe(Me_2[14]tetraenatoN_4)]_2Q]$	8.13 (29), 16.14 (sh, ~2900), 19.88 (6870), 22.0 (8140), 32.0 (17 000)
$[[Fe(Me_2[14]tetraenatoN_4)]_2QCl]$	7.46 (46), 16.6 (sh, 3100), 19.23 (6700), 21.78 (6443), 30.77 (18 560)
$[Fe(Me_2[15]tetraenatoN_4)Cl]$	7.6 (51), 14.9 (sh, ~1040), 18.02 (2225), 22.6 (2517), 30.3 (9440)
$[Fe(Me_2[15]tetraenatoN_4)Br]$	7.7 (54), 14.9 (sh, ~1230), 18.2 (2725), 22.7 (2880), 31.5 (3750)
$[Fe(Me_2[15]tetraenatoN_4)I]$	7.8 (99), 14.6 (sh, ~1500), 18.0 (3000), 22.73 (3805), 34.2 (16 000)
$[Fe(Me_2[15]tetraenatoN_4)NO]$	7.3 (200), 141 (1100), 34.0 (20 800)
$[Fe(Me_2[15]tetraenatoN_4)NCS]$	7.14 (110), 15.4 (sh, 2550), 18.9 (5280), 24.1 (7590), 31.0 (12 000)
$[[Fe(Me_2[15]tetraenatoN_4)]_2Q]$	16.13 (sh, 3490), 19.05 (7160), 22.73 (610), 33.0 (31 120)
$[[Fe(Me_2[15]tetraenatoN_4)]_2QCl]$	16.67 (sh, 4800), 20.0 (6740), 22.73 (8580), 32.26 (27 000)
$[Fe(Me_2[16]tetraenatoN_4)Cl]$	14.08 (1220), 18.42 (2633), 24.1 (2980), 31.75 (15 470)
$[Fe(Me_2[16]tetraenatoN_4)I]$	14.29 (sh, 3017), 16.4 (2740), 23.6 (3464), 34.4 (14 000)
$[[Fe(Me_2[16]tetraenatoN_4)]_2Q]$	18.2 (7451), 23.5 (6065), 32.8 (28 420)
$[[Fe(Me_2[16]tetraenatoN_4)]_2QCl]$	17.33 (9000), 23.3 (6530), 35.2 (42 000)

[a] All spectra were run in $CHCl_3$ solution. Peak maxima are given (10^3 cm^{-1}) followed by approximate extinction coefficients in parentheses.

$toN_4)]_2QCl]$, $\mu_{eff} = 4.41$ μ_B and $\Theta = 51$ K. Both complexes are therefore assumed to have two iron(III) $S = {}^3/_2$ ions in the dimeric complex. Below 30 K these two iron(III) complexes show a substantial deviation from the Curie–Weiss law. This deviation is assumed to arise from a spin–spin coupling interaction between the two $S = {}^3/_2$ iron(III) centers in the dimer. To determine a J value for the spin–spin exchange interaction, the dipolar coupling model of Van Vleck was utilized.[24,26] Using the case of two ions of $S = {}^3/_2$ spin in a dimeric structure gives eq 1 for the magnetic susceptibility

$$\bar{\chi}_A = \frac{N\beta^2\bar{g}^2}{kT}\left[\frac{42 + 15e^{6x} + 3e^{10x}}{7 + 5e^{6x} + 3e^{10x} + e^{12x}}\right] + N\alpha \qquad (1)$$

(atomic) at any temperature, where $x = -J/kT$, $\bar{g}$ is the spectroscopic splitting factor, β is the Bohr magneton, k is the Boltzmann constant, T is temperature, and $N\alpha$ is the temperature-independent paramagnetic term. Calculations of the atomic susceptibility over a temperature range with eq 1 for various values of J and with the assumption that $\bar{g} = 2$ and $N\alpha = 0$ have made it possible to determine the J value for these two complexes. The agreement between the experimental data and the calculated curve for $J = -5.0$ cm^{-1}, as shown in Figure 4 for the 14-membered ring complex $[[Fe(Me_2[14]tetraenatoN_4)]_2QCl]$, is very good. Similarly, the curvature in the $1/\chi_A$ vs. temperature plot for the 15-membered ring complex $[[Fe(Me_2[15]tetraenatoN_4)]_2QCl]$ is also reproduced by using eq 1 with $J = -5$ cm^{-1}. Interestingly, $J = -5$ cm^{-1} observed with these dimeric $S = {}^3/_2$ iron(III) complexes is comparable in magnitude to values of J reported for Cr(III) $S = {}^3/_2$ dimeric complexes.[24]

For the 16-membered ring derivative $[[Fe(Me_2[16]tetraenatoN_4)]_2QCl]$ the variation of $1/\chi_A$ with temperature is linear over the entire temperature range studied (3–359 K). The following values of μ_{eff} and Θ were obtained: $\mu_{eff} = 5.82$ μ_B and $\Theta = 24.5$ K. These results confirm the $S = {}^5/_2$ ground state for this 16-membered ring complex. Since the two 16-membered ring quinonate(2−)-bridged dimeric complexes and the *p*-benzoquinonate(2−)-bridged 15-membered ring dimeric complex $[[Fe(Me_2[15]tetraenatoN_4)]_2Q]$ all have approximately the same magnetic moment at room temperature ($\mu_{eff} \approx 5.6$ μ_B) and since the temperature-dependent susceptibility study for the 16-membered ring complex $[[Fe(Me_2[16]tetraenatoN_4)]_2QCl]$ shows that this complex has the $S = 5/2$ ground state, it is assumed that the other two dimeric complexes also have an $S = {}^5/_2$ ground state. Mössbauer spectral results provide additional support for these assignments for these complexes (vide infra).

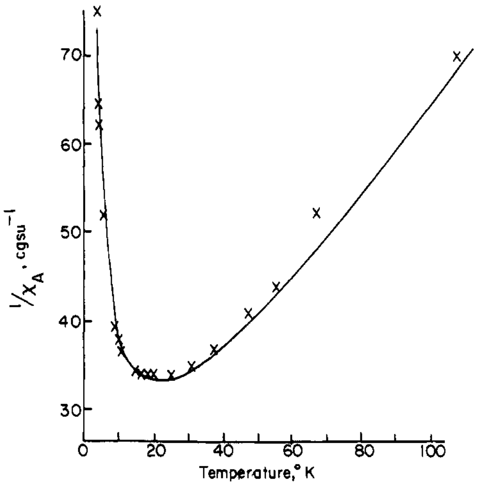

Figure 4. Variation of $1/\chi_A$ with temperature for $[[Fe(Me_2[14]tetraenatoN_4)]_2QCl]$: (×) experimental data; (—) calculated plot.

The three high-spin dimers have lower magnetic moments at room temperature than is expected for high-spin iron(III) ($\mu_{SO} = 5.92$ μ_B). This behavior has been observed for the *p*-benzoquinonate(2−) dimer $[[Fe^{III}(Salen)]_2(p\text{-benzoquinone})]$, which has a reported value of $\mu_{eff} = 5.76$ μ_B at room temperature.[27] The magnetic moment values may be the result of a small interaction between the two iron(III) centers in these dimers. Since there are no deviations from the Curie–Weiss law over the temperature range (3–350 K), any interaction must of necessity be small. To determine a J value for the spin–spin exchange interaction, the dipolar coupling theory of Van Vleck was again utilized.[24-26] Using the case of two ions with $S = {}^5/_2$ spin in a dimeric structure gives eq 2 where $x = -J/kT$. Assuming that $\bar{g} = 2$ and $N\alpha = 0$ gives

$$\bar{\chi}_A = \frac{N\beta^2\bar{g}^2}{kT}\left[\frac{55 + 30e^{10x} + 14e^{18x} + 5e^{24x} + e^{28x}}{11 + 9e^{10x} + 7e^{18x}\; 5e^{24x} + 3e^{28x} + e^{30x}}\right] + N\alpha \qquad (2)$$

an approximate fit to the experimental data when $J = -1$ cm^{-1}. This small value of J manifests itself by a small deviation from the Curie law. This deviation results in a Θ value of 24.5 K for this complex. Thus one can conclude from these studies

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Table IV. Mössbauer Spectral Parameters for the Iron(III) Complexes

compd	spin state, *S*	δ,[a] mm/s	ΔE_q, mm/s	% effect
$[Fe(Me_2[14]tetraenatoN_4)Cl]$	$^3/_2$	0.26	3.19	3.0
$[Fe(Me_2[14]tetraenatoN_4)Br]$	$^3/_2$	0.23	3.53	3.0
$[Fe(Me_2[14]tetraenaoN_4)I]$	$^3/_2$	0.24	3.59	3.1
$[Fe(Me_2[14]tetraenatoN_4)NO]$	$^1/_2$	0.14	2.14	4.2
$[Fe(Me_2[14]tetraenatoN_4)NCS]$	$^3/_2$	0.25	3.25	1.0
$[[Fe(Me_2[14]tetraenatoN_4)]_2Q]$	$^3/_2$	0.28	2.43	2.9
$[[Fe(Me_2[14]tetraenatoN_4)]_2QCl]$	$^3/_2$	0.28	2.85	4.0
$[Fe(Me_2[15]tetraenatoN_4)Cl]$	$^3/_2$	0.27	3.07	1.3
$[Fe(Me_2[15]tetraenaoN_4)Br]$	$^3/_2$	0.28	3.12	1.7
$[Fe(Me_2[15]tetraenatoN_4)I]$	$^3/_2$	0.29	3.25	2.4
$[Fe(Me_2[15]tetraenatoN_4)NO]$	$^1/_2$	0.21	1.86	1.4
$[Fe(Me_2[15]tetraenatoN_4)NCS]$	$^3/_2$	0.28	2.99	3.8
$[[Fe(Me_2[15]tetraenatoN_4)]_2Q]$	$^3/_2$	0.44	0.63	1.5
$[[Fe(Me_2[15]tetraenaoN_4)]_2QCl]$	$^3/_2$	0.38	1.91	2.1
$[Fe(Me_2[16]tetraenatoN_4)Cl]$	$^3/_2$	0.36	2.82	1.3
$[Fe(Me_2[16]tetraenatoN_4)I]$	$^3/_2$	0.38	2.64	2.3
$[[Fe(Me_2[16]tetraenatoN_4)]_2Q]$	$^5/_2$	0.42	0.90	1.7
$[[Fe(Me_2[16]tetraenatoN_4)]_2QCl]$	$^5/_2$	0.42	0.64	1.8

[a] Values with respect to stainless steel; to convert to sodium nitroprusside and 0.16 mm/s.

that the high-spin iron(III) $S = {}^5/_2$ ions are only weakly coupled (if at all) in the *p*-quinone-bridged dimers.

Electronic Spectral Studies. The electronic spectra of all of these new complexes (Table III) are dominated in the visible and near-UV regions by charge-transfer bands. But the low-spin nitrosyl and all the $S = {}^3/_2$ spin complexes do show low-energy bands with extinction coefficients in the range expected for d–d transitions.[29] From theoretical studies it has been shown that certain conditions must be present for the $^4A_2$ state to become the ground state in a d^5 system.[30] Large in-plane ligand fields and tetragonal distortions larger than those used to describe the high-spin ferric porphyrin complexes are required. The low-lying quartet state $^4T_1(O_h)$ can never become the ground state as long as the symmetry of the crystal field is octahedral, but a component of the $^4T_{1g}(^4A_{2g}$ and ^4E_g in $D_{4h})$ can become the ground state when the symmetry of the crystal field is lowered to tetragonal (D_{4h}). For these five-coordinate complexes several observed facts are easily explained in light of these theoretical results. The high-spin compounds are observed only with the weaker in-plane ligands: i.e., the larger 15- and 16-membered rings. When the axial ligand field is large and the tetragonal distortion is lowered, as for the nitrosyl complexes, the ground state is not the $S = {}^3/_2$ but the $S = {}^1/_2$ state. Thus, as the axial field strength is weakened, the $^4A_{2g}$ state becomes the ground state on going to the limit of planar four-coordination.[30] Anisotropic magnet susceptibility measurements on a single crystal of the square-planar phthalocyaninato manganese(II) complex[32] that contains the d^5 Mn(II) ion in the intermediate-spin $S = {}^3/_2$ ground state support these assignments and show that the magnetic anisotropy is consistent with a $^4A_{2g}$ ground state.[31]

Mössbauer Spectra of the Iron(III) Complexes. In all cases the Mössbauer spectra (Table IV) of the Fe(III) complexes consist of a single quadrupole-split doublet, with no evidence of iron contaminants. The isomer shift values for these complexes are in the range usually found for Fe(III) complexes,[32] with the high-spin Fe(III) derivatives having the highest values (lowest electron density at the nucleus) in the range 0.42–0.44 mm/s with respect to stainless steel. The low-spin derivatives have the lowest value, 0.14 and 0.21 mm/s, while the intermediate-spin $S = {}^3/_2$ complexes have isomer shift values between the two extremes, ranging from 0.23 to 0.38 mm/s.

The five-coordinate Fe(III) complexes also show a macrocyclic ring size effect on the isomer shift. Once again, the smaller the macrocyclic ligand the better it is as a σ donor.[33] This results in lower δ values (greater s-electron density at the nucleus). For example, the two low-spin nitrosyl adducts have an 0.07 mm/s difference in the δ values; the smaller δ value corresponds to the smaller ring. This trend is not as dramatic within the series of $S = {}^3/_2$ complexes, since the 14- and 15-membered ring derivatives have similar δ values, but the δ differences between the 14- and 16-membered ring iodo or chloro complexes is substantial and confirms the notion that the smaller rings exhibit greater ligand field strengths on iron(III).

The quadrupolar splitting values for these complexes are very informative and have helped to confirm spin-state assignments for some of these new Fe(III) complexes. For example, the three quinonate(2−)-bridged dimers that were assigned the $S = {}^5/_2$ ground state have the lowest ΔE_q values observed for these Fe(III) complexes. Since high-spin Fe(III) has a spherically symmetrical d-electron population, high-spin Fe(III) complexes have atypically small ΔE_q values; thus, the lower values observed for these complexes agree with the $S = {}^5/_2$ ground-state assignment. The splittings observed for these complexes must then be predominantly due to the ligand asymmetry around the Fe(III) nucleus. It has been demonstrated for five-coordinate high-spin iron(II) complexes that the five-coordination can result in a large ligand field contribution to the net electric field gradient.[34] Thus, it is expected that these five-coordinate high-spin Fe(III) complexes would exhibit quadrupole splittings due to the asymmetric ligand environment. The two low-spin Fe(III) nitrosyl complexes have ΔE_q values that are approximately 1.1 mm/s greater than the splittings observed for the high-spin Fe(III) complexes. This increased splitting is expected since low-spin Fe(III) has one unpaired electron in the $t_{2g}(O_h)$ set of orbitals. Thus, both electronic and ligand field factors can contribute to the electric field gradient. Even larger splittings are observed for the remaining $S = {}^3/_2$ ground-state complexes. The values for these $S = {}^3/_2$ derivatives range from 1.91 to 3.59 mm/s, within the range observed for other $S = {}^3/_2$ complexes. For example, the ferric porphyrin derivatives[8,9,10b] have ΔE_q values in this range, ferric phthalocyanine chloride has value of 2.51 mm/s,[35] and for a somewhat similar five-coordinate macrocyclic Fe(III) complex with a 16-membered ligand ΔE_q is reported to be 1.93 mm/s.[6]

Within the series of $S = {}^3/_2$ complexes reported here, the largest values of the quadrupole splitting are observed for the complexes with smaller rings (keeping the axial ligand constant for comparison). If the ligand field contributions to the electric field gradient are the same sign, then one might expect to observe this trend since the smaller rings would exert a larger ligand field, thus resulting in a greater tetragonal distortion.

Conclusions. In an earlier study we showed that the square-planar ($S = 1$) iron(II) complexes **1a–c** are susceptible to electrophilic attack on the center carbons of the charge-delocalized six-membered chelate rings.[2] The work reported here has more completely defined the conditions under which ligand reactions (addition or oxidation) or metal oxidation will take place. With relatively mild oxidizing agents, one-electron oxidation of the Fe(II) center takes place, forming five-coordinate Fe(III) complexes. With stronger (less selective)

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oxidants, competing ligand oxidation reactions apparently take place, although no pure products could be isolated to confirm this.

One feature that stands out in this series of Fe(III) complexes is the effect of ring size and axial donor on the spin state of the Fe(III) ion. A vivid example of the effect of the axial donor is exhibited by the two 15-membered ring *p*-quinonate(2–)-bridged dimer derivatives. The Fe(III) centers in the benzoquinone derivative are in the $S = {}^5/_2$ ground spin state, while the Fe(III) centers in the tetrachlorobenzoquinone derivative are in the $S = {}^3/_2$ ground state. Interestingly, these *p*-quinonate(2–) derivatives may possibly serve as models for the cytochrome type dehydrogenases in which a coenzyme, a *p*-quinone derivative, is known to donate electrons to the iron in the heme group of the cytochrome.

In light of our results and those of other workers,[6] it is likely that the $S = {}^3/_2$ ground spin is common for Fe(III) bound to N_4X donor sets. Further, this $S = {}^3/_2$ ground state may be relevant for intermediates in the biological reactions of heme iron derivatives, such as the cytochromes.[9c]

Acknowledgment. We wish to thank Dr. John A. Stone of the Savannah River Laboratory (E. I. du Pont de Nemours and Co., Inc.) for his assistance in obtaining the Mössbauer spectra. Further, we want to thank Dr. David Karraker (Savannah River Laboratory) for his assistance in obtaining the low-temperature magnetic susceptibility data. Support by the National Institutes of Health is appreciated.

Registry No. **1a**, 62158-22-9; **1b**, 62158-23-0; **1c**, 62158-25-2; [Fe(Me$_2$[14]tetraenatoN$_4$)Cl], 91294-67-6; [Fe(Me$_2$[14]tetraenatoN$_4$)Br], 91294-68-7; [Fe(Me$_2$[14]tetraenatoN$_4$)I], 91294-69-8; [Fe(Me$_2$[14]tetraenatoN$_4$)(NO)], 91294-70-1; [Fe(Me$_2$[14]tetraenatoN$_4$)(NCS)], 91294-71-2; [[Fe(Me$_2$[14]tetraenatoN$_4$)]$_2$Q], 91294-72-3; [[Fe(Me$_2$[14]tetraenatoN$_4$)]$_2$QCl], 91294-73-4; [Fe(Me$_2$[15]tetraenatoN$_4$)Cl], 91294-74-5; [Fe(Me$_2$[15]tetraenatoN$_4$)Br], 91294-75-6; [Fe(Me$_2$[15]tetraenatoN$_4$)I], 91294-76-7; [Fe(Me$_2$[15]tetraenatoN$_4$)(NO)], 91294-77-8; [Fe(Me$_2$[15]tetraenatoN$_4$)(NCS)], 91294-78-9; [[Fe(Me$_2$[15]tetraenatoN$_4$)]$_2$Q], 91294-79-0; [[Fe(Me$_2$[15]tetraenatoN$_4$)]$_2$QCl], 91294-80-3; [Fe(Me$_2$[16]tetraenatoN$_4$)Cl], 91294-81-4; [Fe(Me$_2$[16]tetraenatoN$_4$)I], 91294-82-5; [[Fe(Me$_2$[16]tetraenatoN$_4$)]$_2$Q], 91310-94-0; [[Fe(Me$_2$[16]tetraenatoN$_4$)]$_2$QCl], 91310-95-1.

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Reactions of Metal Atoms with Alkynes. 2.[1] Cocondensation Reactions of Germanium and Tin Atoms with Acetylene and Formation of Integral Metal–Acetylene Polymers

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Received November 22, 1983

Germanium and tin vapors react with acetylene in a stationary metal atom reactor to form integral acetylene–metal copolymers of reproducible stoichiometry, i.e. $(C_2H_{2.7}Ge_{0.72})_x$ and $(C_2H_{2.6}Sn_{0.70})_x$. The metal is incorporated as M(II) and M(IV) species, and the resultant materials are air-sensitive and possess moderate free-radical concentrations but are nonconducting under normal pressed-powder conditions.

Introduction

In 1978 we reported that germanium vapor, when cocondensed with either propyne or but-2-yne in a synthetic-scale metal atom reactor, yielded high polymers (containing *incorporated germanium*) that were unreactive toward concentrated hydrochloric acid and room-temperature aqua regia and were insoluble in common organic solvents.[1] Due to the difficulty in characterizing these polymeric substances, no further work has been performed on either the propyne or but-2-yne reaction products.

Recently, the ability of (suitably doped) polyacetylenes to conduct electric current[2] has rekindled our interest in the interaction of metal vapors with alkynes. Specifically, we wished to investigate the polymerization of acetylene by germanium and tin vapors to determine (a) whether polymerization would occur and (b) whether the metal atoms would simultaneously act as polymerization initiators and polymer dopants. Indeed, we have found that both germanium and tin atoms/vapors react with acetylene in a unique manner when compared to other metal vapors, producing interesting new materials. Herein we report the synthesis and properties of these polymers.

Experimental Section

Metal Atom Reactor. The design of the simple metal atom reactor, which is the basis for the reactions herein described, has been detailed elsewhere.[3] Due to the volatility of acetylene, however, the "shower head" ligand inlet was modified to permit more efficient metal–acetylene mixing during the cocondensation process. This modified system is fashioned with ~1-mm holes that extend about 20 mm up from the bottom of the shower head. This small area of holes (the normal area of holes extends about 90 mm up from the bottom of the shower head) was necessitated by the volatility of the gaseous acetylene being inlet to the reaction zone. With this design, condensation of the acetylene on the reactor walls is very efficient, ensuring that the low pressures necessary for a successful metal atom reaction are easily maintained and that the acetylene remains in the reactor and is not pumped away during the course of a reaction. A silicone oil bubbler fitted with a needle valve is used to control the acetylene inlet rate.

Acetylene Purification. *Caution*! Acetylene gas should always be handled in glass and/or aluminum, stainless-steel, or other nonreactive tubing. Prolonged contact with copper tubing is especially to be avoided. Handling of acetylene at greater than atmospheric pressure is also to be avoided, since even small pressures above atmospheric pressure (as little as 30 psia in a 1-in. tube, or smaller over-pressures in larger volumes) can cause spontaneous deflagration or detonation.[4] Care must be taken to ensure that the final pressure of acetylene gas

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