spectra,[27] and final converged values are listed in Table IV. Double-ζ Slater orbitals were used to represent the d orbitals, and single-ζ Slater orbitals were used for s and p orbitals.

No attempt was made to fit our calculated results to other results or experimental data. The secular equation was solved by using the standard Wolfsberg-Helmholz[28] formula for off-diagonal terms (eq 1). The parameters used for cluster

$$H_{ij} = \tfrac{1}{2}KS_{ij}(H_{ii} + H_{jj}) \qquad K = 1.75 \tag{1}$$

calculations were then employed for bulk calculations through the use of Bloch functions, by using procedures described in earlier work.[12] The bond length in all clusters and the bulk was 2.5 Å.

The density-of-states curves were calculated by using Gaussian functions of 0.1 eV fwhm. These functions were centered on each energy level and summed. The normalized sums were then plotted as the density of states. Binding energies were calculated as energy differences between cluster and all of the isolated atoms by using eq 2, where E = energy,

$$E = \sum_i E_i N_i \tag{2}$$

E_i = energy of molecular orbital i, and N_i = occupation, as in standard calculations.[9] A Mulliken-type analysis[29] was used to determine the orbital populations.

Registry No. Ag, 7440-22-4; Au, 7440-57-5; Pd, 7440-05-3; Ru, 7440-18-8; Rh, 7440-16-6; $Rh_6(CO)_{16}$, 28407-51-4.

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Spin-Crossover Ferric Complexes: Curiosities Observed for Unperturbed Solids

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The preparation and characterization of a series of spin-crossover ferric complexes with the composition $[Fe(X\text{-}SalEen)_2]Y$, where X-SalEen results from the Schiff-base condensation of X-substituted salicylaldehyde and *N*-ethylethylenediamine, are reported. Several of the complexes exhibit a gradual, but complete, spin-crossover transition from high spin to low spin in the solid state, whereas certain complexes exhibit an incomplete transition and there is a "plateau" in the μ_{eff}/Fe vs. temperature curve. One compound, $[Fe(3\text{-}OCH_3\text{-}SalEen)_2]PF_6$, experiences a sudden spin-crossover phase transition. The conversion from high spin to low spin occurs within a 2° range around the temperature 159 K. A sensitivity of physical properties to exact compound preparation is demonstrated. In spite of the variation in the series, it is shown by variable-temperature ^{57}Fe Mössbauer and EPR techniques that only two electronic states, the high-spin $^6A_1$ excited state and one low-spin Kramers doublet ground state, are thermally populated for any of the compounds. There is no evidence of an intermediate-spin state. The ground-state Kramers doublet in these complexes has one unpaired electron in an orbital which is largely d_{xy} in composition.

Introduction

Several iron(II) and iron(III) complexes exhibit properties characteristic of "spin-equilibrium" complexes, where a high-spin excited state is within thermal energy of the low-spin ground state.[3] Many studies have focused on determining the types of ligands that lead to a "spin-equilibrium" complex and whether ligand substituents affect the equilibrium. Only very recently has there been significant progress in answering a fundamental yet more difficult question, namely: What are the kinetics and mechanisms of spin state interconversions? Spin transitions are believed to play an important role in biological systems, and spin equilibria in certain hemoproteins may be coupled to electron transport.[4] For spin-crossover iron complexes in solution, magnetic susceptibility data yield approximately linear log K vs. $1/T$ plots, consistent with a dynamic equilibrium between the two spin states where K is the equilibrium constant. In fact, relaxation techniques have been used to measure "spin-flipping" rates for complexes in solution.[5-7]

"Spin-equilibrium" compounds in the solid state seldom give linear plots of log K vs. $1/T$. Several curiosities have been observed for spin-crossover iron(II) and iron(III) complexes in the solid state. First, the variation of the effective magnetic moment (μ_{eff}) per iron ion (or molar paramagnetic susceptibility) vs. temperature for a given complex does not correspond simply to a Boltzmann distribution over the thermally populated high-spin and low-spin states. For the ferric dithiocarbamate spin-crossover complexes, for example, *apparently* successful theoretical fits of the susceptibility data could only be obtained by assuming a temperature-dependent energy separation between the high-spin and low-spin states together with a temperature-dependent vibrational partition coefficient.[8] Infrared data, however, do not support such assumptions.[8,9] Almost discontinuous (i.e., occurring over a few degrees) high-spin to low-spin transitions have been noted for a number of iron(II) complexes,[10] which could also be a manifestation of something more than a simple Boltzmann distribution.

A second curiosity observed in the solid state for spin-crossover complexes is an incompleteness of the transition at

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low temperatures. In the case of a complete transition for a spin-crossover iron(III) complex, μ_{eff}/Fe would be expected to vary as the temperature of the complex is descreased from a value of ca. 5.9 μ_B appropriate for the high-spin state to ca. 2.0 μ_B which is characteristic of the low-spin state. Several spin-crossover iron(III) complexes do not exhibit such a change, but instead μ_{eff}/Fe decreases to an intermediate value at some temperature and further reduction of the sample temperature does not lead to a change in μ_{eff}/Fe. A "plateau" in the μ_{eff}/Fe vs. temperature curve is seen for [Fe(4-OCH_3-Salmeen)$_2$]PF_6, where 4-OCH_3-Salmeen is the monoanion of the condensation product of 4-methoxysalicylaldehyde and *N*-methylethylenediamine.[11] A gradual drop of μ_{eff}/Fe from 5.76 μ_B at 298.4 K to 4.37 μ_B at 18.0 K with an essentially constant moment below 100 K is seen for this compound. Other iron(III) complexes exhibit plateaus in the μ_{eff}/Fe vs. temperature curves,[12,13] and in the case of an iron(III) dithiocarbamate complex the plateau was attributed to a $^6A_1 \rightleftharpoons {}^4T_1$ rather than a $^6A_1 \rightleftharpoons {}^2T_2$ conversion (i.e., an intermediate-spin ground state).[13] Several spin-crossover iron(II) complexes also show incomplete transitions. One of the iron(II) systems studied most thoroughly is [Fe(2-pic)$_3$]X_2·S, where 2-pic is 2-aminomethylpyridine, X is Cl^-, Br^-, or I^-, and S is CH_3OH, C_2H_5OH, or nothing.[14-19] A relatively sharp transition from essentially high spin to essentially low spin is observed for the unsolvated chloride complex. The unsolvated bromide and iodide salts, however, show a plateau in the μ_{eff}/Fe vs. temperature curves. Upon solvating of the bromide and iodide salts a complete transition is seen.

Probably the first significant step to understand the nature of spin-crossover transitions observed in the solid state was made by Sorai and Seki.[20] Heat capacity and variable-temperature infrared and far-infrared measurements were carried out on [Fe(phen)$_2$(NCS)$_2$] and [Fe(phen)$_2$(NCSe)$_2$] to find that the spin-crossover transition is a first-order phase transition and the difference in entropy between the two spin states is the driving force. It was suggested that the spin transition in these complexes is a cooperative phenomenon and occurs via significant coupling between the electronic structure of the metal ion and the phonon system consisting of intramolecular and intermolecular vibrations. It was further suggested that the spin-crossover transition involves the formation of a domain (small region) of low-spin molecules in a crystallite of the high-spin phase. The size of the low-spin domains affects the degree of cooperativity and therefore the shape of the μ_{eff}/Fe vs. temperature curve. A sudden transition is characterized by appreciable cooperativity. Sorai and Seki[20] used a phenomenological model to calculate the low-spin domain size for [Fe(phen)$_2$(NCS)$_2$] as 70–100 molecules. Very recently Gütlich et al.[21] also used a phenomenological thermodynamic model to fit the ^{57}Fe Mössbauer data for [Fe_xZn_{1-x}(2-pic)$_3$]Cl_2·C_2H_5OH ($1.0 \geq x \geq 0.0009$). They found the average domain size for the pure iron compound to be ca. 3.5 molecules and that the size decreases with decreasing iron concentration.

The above phenomenological models do not explicitly account for the observation of incomplete spin-crossover transitions and other pecularities in μ_{eff}/Fe vs. temperature curves, as well as the sensitivity of the spin-crossover phenomenon to solvation and sample preparation. It is our hypothesis that all of the curiosities observed for solid-state spin-crossover complexes can be explained by the general nucleation and growth mechanism of phase transitions in solids.[22,23] In many cases there is probably kinetic control on the spin-crossover phase transition. In this regard, it is important to note that Goodwin and Smith[24] observed that annealing [Fe^{II}(L)$_2$]BF_4 (L = phen or bpy), for which there is a plateau at 3.89 μ_B in the μ_{eff}/Fe vs. temperature curve, leads to a time-dependent decrease of the magnetic moment. For example, a dramatic effect was seen with the sample at 83 K where μ_{eff}/Fe decreased from 3.89 to 1.89 μ_B after a period of 50 weeks. König and co-workers[25] recently reported ^{57}Fe Mössbauer data for an iron(II) compound that exhibits a pronounced hysteresis in the spin-crossover transition. They found that cooling the sample rapidly left many of the molecules in the high-spin state compared to a sample which was cooled slowly. The rapidly cooled sample slowly transformed to the "equilibrium" composition, which allowed a determination of the rate of conversion in the solid state.

According to the nucleation and growth mechanism[22,23] of phase transitions in solids, the transformation from high spin to low spin would involve the formation of small regions (i.e., domains) of the low-spin phase in a high-spin crystallite and the subsequent growth of the domains. The rate of growth of critical-size domains of low-spin molecules determines the nature of the spin-crossover phase transition. The first objective in the present study was to prepare a series of spin-crossover iron(III) complexes that not only did not tend to solvate but also exhibited the full range of curiosities. Iron(III) complexes were desirable, because not only could ^{57}Fe Mössbauer and magnetic susceptibility measurements be carried out but also the complexes could be investigated with EPR spectroscopy. Some of the results of this study have been communicated.[26] In the following paper, the compounds will be examined for evidence of the nucleation and growth mechanism.

Experimental Section

Physical Measurements. Variable-temperature (4.2–286 K) magnetic susceptibility data were obtained by using a Princeton Applied Research Model 150A vibrating-sample magnetometer operating at 13.75 kG and calibrated with $CuSO_4$·$5H_2O$ as described in a previous paper.[27] All data were corrected for compound diamagnetism.[28]

ESR spectra were obtained with a Varian E-9 X-band spectrometer equipped with a Varian temperature controller (80–380 K). An Oxford Instruments helium-flow accessory was used in the temperature range of 3.2–80 K.

Iron-57 Mössbauer measurements were obtained with a constant acceleration instrument which has been described.[29] Computer fittings

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of the data to Lorentzian lines were carried out with a modified version of a previously reported program.[30]

Compound Preparation. All elemental analyses were performed in the Microanalytical Laboratory of the School of Chemical Sciences. The ligands used in this study are the Schiff-base condensation products of *N*-ethylethylenediamine (Ames Laboratories) with either salicylaldehyde, 3-methoxysalicylaldehyde, or 5-methoxysalicylaldehyde, which were used as commercially available from Aldrich. The ligands obtained in these three cases are SalEen, 3-OCH_3-SalEen, or 5-OCH_3-SalEen, respectively.

[Fe(3-OCH_3-SalEen)$_2$]NO_3·$^1/_2H_2O$. The yellow Schiff-base solution was formed by adding 3.04 g of 3-methoxysalicylaldehyde dissolved in 30 mL of CH_3OH to 30 mL of CH_3OH in which *N*-ethylethylenediamine (1.76 g) is dissolved. Sodium hydroxide (0.84 g) dissolved in 10 mL of H_2O is then added. A 40-mL CH_3OH solution of 4.0 g of $Fe(NO_3)_3·9H_2O$ is added slowly to the stirring solution. When the last of the ferric nitrate solution is added, a massive greenish microcrystalline product precipitates. The product is collected on a glass frit, washed with ether, and then dried in vacuo over P_4O_{10}. Anal. Calcd for $C_{24}H_{35}N_5O_{7.5}Fe$: C, 50.65; H, 6.15; N, 12.30; Fe, 9.81. Found: C, 50.70; H, 6.27; N, 12.58; Fe, 9.68.

[Fe(3-OCH_3-SalEen)$_2$]PF_6. Samples of [Fe(3-OCH_3-SalEen)$_2$]PF_6 were prepared by metathesis of the above NO_3^- salt in CH_3OH. A typical procedure would involve dissolving 0.9 g of the NO_3^- salt in 50 mL of boiling CH_3OH. A twofold excess of $NaPF_6$ dissolved in 15–20 mL of CH_3OH is then added. The solution is then filtered and cooled in a refrigerator to precipitate a black microcrystalline product. Three different samples, labeled 1, 3, and 4, were prepared in the above manner. Preparation 2 of this compound is described below. Anal. Calcd for $C_{24}H_{34}N_4O_4FePF_6$: C, 44.83; H, 5.29; N, 8.71; Fe, 8.68. Found: C, 44.85; H, 5.32; N, 8.70; Fe, 8.64.

Preparation 2 of [Fe(3-OCH_3-SalEen)$_2$]PF_6 was carried out in the hope of obtaining a noncrystalline sample. The procedure followed was the same as that used for the NO_3^- salt. In this case, however, ca. 2.0 g of $NaPF_6$ was dissolved in the Schiff-base solution to give a cloudy solution, and the $Fe(NO_3)·9H_2O$ solution was then added. An apparently noncrystalline black precipitate separated. The powder was collected on a frit and then stirred in 10 mL of H_2O for 5 min to dissolve any $NaPF_6$ left in the product. If the cloudy $NaPF_6$ Schiff-base solution is filtered before the $Fe(NO_3)·9H_2O$ solution is added, a microcrystalline PF_6^- salt precipitates. The noncrystalline-appearing powder was analyzed and studied as preparation 2. Anal. Calcd for $C_{24}H_{34}N_4O_4FePF_6$: C, 44.83; H, 5.29; N, 8.71; Fe, 8.68. Found: C, 44.70; H, 5.28; N, 8.71; Fe, 9.02.

[Fe(3-OCH_3-SalEen)$_2$]BPh_4. This compound was made by the metathesis of the NO_3^- salt with $NaBPh_4$ in methanol. It is important that less than a stoichiometric amount of $NaBPh_4$ be used to get a microcrystalline black product. Anal. Calcd for $C_{48}H_{54}N_4O_4FeB$: C, 70.51; H, 6.60; N, 6.85; Fe, 6.83. Found: C, 70.34; H, 6.72; N, 6.86; Fe, 6.60.

[Fe(SalEen)$_2$]NO_3. The same procedure that was used for [Fe(3-OCH_3-SalEen)$_2$]NO_3 was used to prepare this compound, except in this case 2.44 g of salicylaldehyde is used in place of the 3-methoxysalicylaldehyde. The compound [Fe(SalEen)$_2$]NO_3 is more soluble in CH_3OH than in the 3-methoxy analogue; hence it does not precipitate as rapidly. Two preparations (1 and 2) of this compound were made. Anal. Calcd for $C_{22}H_{30}N_5O_5Fe$: C, 52.84; H, 6.00; N, 14.00; Fe, 11.17. Found for preparation 2: C, 52.92; H, 6.00; N, 13.75; Fe, 11.26.

[Fe(SalEen)$_2$]PF_6. Metathesis of the corresponding NO_3^- salt with $NaPF_6$ in methanol was used to prepare this compound. Anal. Calcd for $C_{22}H_{30}N_4O_2FePF_6$: C, 45.32; H, 5.12; N, 9.60; Fe, 9.58. Found: C, 45.05; H, 5.17; N, 9.60; Fe, 9.37.

[Fe(SalEen)$_2$]BPh_4·$^1/_2H_2O$. One gram of the NO_3^- salt was dissolved in 50 mL of CH_3OH. A solution of 0.55 g of $NaBPh_4$ in 25 mL of CH_3OH was added slowly to effect the precipitation of a dark brown microcrystalline compound. Anal. Calcd for $C_{46}H_{51}N_4O_{2.5}FeB$: C, 72.11; H, 6.66; N, 7.31; Fe, 7.29. Found: C, 72.17; H, 6.84; N, 7.44; Fe, 7.23.

[Fe(5-OCH_3-SalEen)$_2$]NO_3. This compound was prepared in a manner similar to that for the compound [Fe(3-OCH_3-SalEen)$_2$]NO_3. The first microcrystalline black solid that precipitated did not give a good analysis for iron; consequently the solid was redissolved in CH_3OH and the solution filtered to remove suspended ferric oxide or hydroxide impurity. The filtered solution was then evaporated to dryness with a rotovap to give a black microcrystalline product. Anal. Calcd for $C_{24}H_{34}N_4O_7Fe$: C, 51.46; H, 6.07; N, 12.50; Fe, 9.97. Found: C, 51.72; H, 6.25; N, 12.53; Fe, 10.17.

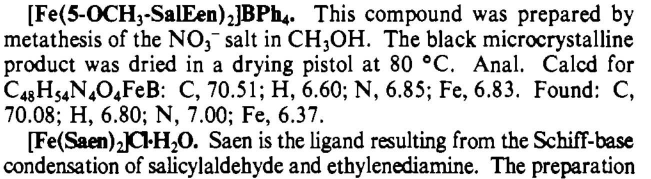
[Fe(5-OCH_3-SalEen)$_2$]$(PF_6)_{0.5}(NO_3)_{0.5}$. Metathesis of the corresponding NO_3^- salt in CH_3OH failed to give a pure sample of the PF_6^- salt, but instead the mixed anion salt was always obtained. Anal. Calcd for $C_{24}H_{34}N_{4.5}O_{5.5}P_{0.5}F_3Fe$: C, 47.92; H, 5.65; N, 10.47; Fe, 9.28. Found: C, 47.08; H, 5.42; N, 10.77; Fe, 8.92.

[Fe(5-OCH_3-SalEen)$_2$]BPh_4. This compound was prepared by metathesis of the NO_3^- salt in CH_3OH. The black microcrystalline product was dried in a drying pistol at 80 °C. Anal. Calcd for $C_{48}H_{54}N_4O_4FeB$: C, 70.51; H, 6.60; N, 6.85; Fe, 6.83. Found: C, 70.08; H, 6.80; N, 7.00; Fe, 6.37.

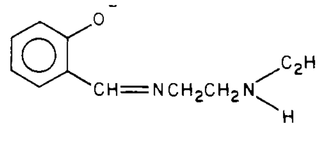
[Fe(Saen)$_2$]Cl·H_2O. Saen is the ligand resulting from the Schiff-base condensation of salicylaldehyde and ethylenediamine. The preparation of this iron complex has been reported previously.[31] A different synthetic procedure, however, was employed in this work. Salicylaldehyde (2.41 g), ethylenediamine (0.84 g), and sodium hydroxide (0.84 g) were reacted in 50 mL of CH_3OH. A methanolic solution of $FeCl_3·6H_2O$ (2.70 g) was slowly added to the clear yellow Schiff-base solution. The resulting dark purple solution was filtered and the filtrate cooled in a refrigerator. The product was obtained in two crops. The second crop to precipitate gave the better analysis. Anal. Calcd for $C_{18}H_{24}N_4O_3Fe$: C, 49.30; H, 5.47; N, 12.77; Fe, 12.74. Found: C, 49.23; H, 5.65; N, 12.68; Fe, 12.55.

Results and Discussion

Compound Preparation and Structure. Pseudooctahedral complexes of Fe(III) with an N_4O_2 coordination core were prepared, employing as a ligand the Schiff-base condensation product of salicylaldehyde, 3-methoxysalicylaldehyde, or 5-methoxysalicylaldehyde with *N*-ethylethylenediamine. Each ligand is deprotonated to give a monoanionic tridentate N_2O ligand. The overall reaction is



The anions used are NO_3^-, PF_6^-, and BPh_4^-, and the ligand X-SalEen is represented as



In the absence of a single-crystal X-ray structure determination it is difficult to tell whether the tridentate X-SalEen$^-$ ligands are disposed about the Fe(III) ion in a facial or meridional configuration. A crystal structure was recently reported[31] for bis[*N*-(2-aminoethyl)salicylaldiminato]iron(III) chloride monohydrate, [Fe(Saen)$_2$]Cl·H_2O, where Saen$^-$ results from the Schiff-base condensation of salicylaldehyde and ethylenediamine. The two Saen$^-$ ligands are coordinated in a meridional configuration. The physical properties of [Fe(Saen)$_2$]Cl·H_2O are very similar to those of the [Fe(X-SalEen)$_2$]Y compounds. The low-spin compound [Fe(Saen)$_2$]Cl·H_2O shows a single quadrupole-split doublet in the ^{57}Fe Mössbauer spectrum with a quadrupole splitting of ΔE_Q = 2.75 mm/s,[31] in excellent agreement with the values obtained (vide infra) for the [Fe(X-SalEen)$_2$]Y compounds. An EPR spectrum was recorded for a solid sample of [Fe(Saen)$_2$]Cl·H_2O. The rhombic signal is characterized by *g* values of

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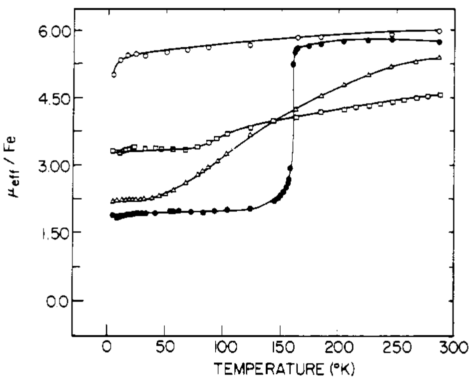

Figure 1. Plots of effective magnetic moment per iron ion, μ_{eff}/Fe, vs. temperature: $[Fe(3\text{-}OCH_3\text{-}SalEen)_2]PF_6$, ●; $[Fe(SalEen)_2]PF_6$, △; $[Fe(SalEen)_2]NO_3$, preparation 2, □; $[Fe(3\text{-}OCH_3\text{-}SalEen)_2]BPh_4$, ○.

2.213, 2.146, and 2.005, which again indicates that this complex is isostructural to the $[Fe(X\text{-}SalEen)_2]Y$ compounds. If you add to this the fact that the analogous Co(III) and Cr(III) complexes have also been shown with structural work[32,33] to be meridional, it is likely that the $[Fe(X\text{-}SalEen)_2]Y$ compounds are meridional.

Magnetic Susceptibility. The initial goal of preparing a series of spin-crossover ferric complexes that exhibit the full range of curiosities in μ_{eff}/Fe vs. temperature curves was realized with the $[Fe(X\text{-}SalEen)_2]Y$ compounds. Magnetic susceptibility data (4.2–286 K) are given in Tables I–XI.[34] Figure 1 shows the variation with temperature of the effective magnetic moment per iron ion for four of the compounds. One preparation (preparation 2, Table II[34]) of the compound $[Fe(SalEen)_2]NO_3$ exhibits a decrease in μ_{eff}/Fe from 4.50 μ_B at 286 K to 3.26 μ_B at 4.2 K. The transition is incomplete, and, as can be seen in Figure 1, there is a "plateau" in μ_{eff}/Fe at a value of ca. 3.3 μ_B when the sample temperature is less than 80 K. The second sample (preparation 1, Table I[34]) of this same compound also shows a plateau at about the same value of μ_{eff}/Fe; however, μ_{eff}/Fe is 4.79 μ_B at 286 K for this sample. As observed by others, the properties of spin-crossover complexes vary from one sample preparation to another.

A change in the anion gives $[Fe(SalEen)_2]PF_6$ which exhibits a "normal" gradual spin-crossover transition (see Figure 1). Two different samples of $[Fe(SalEen)_2]PF_6$ were prepared, and both were found to undergo a very nearly complete transition wherein μ_{eff}/Fe decreases to a value of ca. 2.1 μ_B at 4.2 K. A value of ca. 2.0 μ_B is characteristic of an Fe(III) complex in a low-spin state; a value of 5.9 μ_B would be expected for an Fe(III) complex in a high-spin state. The two different preparations of $[Fe(SalEen)_2]PF_6$ do *not* have superimposable μ_{eff}/Fe vs. temperature curves, but preparation 1 has 5.56 μ_B at 286 K compared to a value of 5.31 μ_B for preparation 2.

The compound $[Fe(3\text{-}OCH_3\text{-}SalEen)_2]PF_6$ plays a crucial role in this study, for it is the only complex which undergoes a relatively sudden transition from essentially high spin to essentially low spin around T_c = ca. 159 K (T_c is the temperature at which there are equal amounts of high-spin and low-spin molecules). The conversion occurs within ca. 2 K (see Figure 1). Four different samples of this compound were prepared, and the three microcrystalline samples all exhibited the sudden transition. In the case of preparation 1, for example, the value of μ_{eff}/Fe at 158.8 K is 5.17 μ_B and drops to 2.88 μ_B at 157.1 K (see Table V[34]). Preparation 2 of $[Fe(3\text{-}OCH_3\text{-}SalEen)_2]PF_6$ was isolated by rapid precipitation and did not visually appear to be microcrystalline. The spin-crossover phase transition for this sample was found to be more gradual than for the other samples, and examination of Table VI[34] shows that there is a low-temperature plateau in the μ_{eff}/Fe vs. temperature curve with a value of ca. 2.70 μ_B. The other three samples have μ_{eff}/Fe values less than 2.0 μ_B at 4.2 K, which is diagnostic of a complete transition.

Substitution of BPh_4^- for the PF_6^- counterion in the case of the 3-methoxy-substituted compound leads to a dramatic change as indicated in Figure 1 (Table IX[34]). There is a gradual decrease in μ_{eff}/Fe from 5.92 μ_B at 286 K to 4.95 μ_B at 4.2 K for $[Fe(3\text{-}OCH_3\text{-}SalEen)_2]BPh_4$. In the absence of the physical properties that are described in later sections of this paper, it would be tempting to ascribe this gradual decrease to single-ion zero-field splitting. As can be seen in Figure 1, the gradual decrease in μ_{eff}/Fe occurs across the full temperature range. This is not characteristic of zero-field splitting. Spectroscopic data (vide infra) indicate the presence of not only high-spin molecules but also low-spin molecules as well.

The magnetic susceptibility data for the four remaining compounds are not illustrated (see Tables X and XI[34]). The compounds $[Fe(3\text{-}OCH_3\text{-}SalEen)_2]NO_3\cdot{}^1/_2H_2O$ and $[Fe(5\text{-}OCH_3\text{-}SalEen)_2]NO_3$ are both essentially low-spin complexes, whereas $[Fe(SalEen)_2]BPh_4\cdot{}^1/_2H_2O$ is a high-spin complex. The mixed-anion compound $[Fe(5\text{-}OCH_3\text{-}SalEen)_2](NO_3)_{0.5}(PF_6)_{0.5}$ is a spin-crossover complex (Table X[34]), where μ_{eff}/Fe varies from 4.02 μ_B at 286 K to 1.88 μ_B at 44.1 K. It appears that in the $[Fe(X\text{-}SalEen)_2]Y$ series the BPh_4^- counterion tends to give a high-spin complex, the NO_3^- counterion tends to give a low-spin complex, and the PF_6^- counterion gives complexes which undergo the spin-crossover transition. There is an appreciable variability of properties from one sample preparation to another for a given compound.

Mössbauer Spectroscopy. Iron-57 Mössbauer data have been accumulated for five of the compounds between room temperature and liquid-nitrogen temperature, and some of these data are given in Table XII. Four important conclusions can be made from the Mössbauer data.

First of all, it is clear from all of the data that only two electronic states are thermally populated in the $[Fe(X\text{-}SalEen)_2]Y$ compounds, one Kramers doublet from the $^2T_{2g}$ state and the $^6A_{1g}$ state. Figure 2 illustrates spectra obtained for two of the 3-methoxy-substituted compounds. The compound $[Fe(3\text{-}OCH_3\text{-}SalEen)_2]PF_6$ undergoes a sudden spin-crossover transition and in tracing A is given a spectrum of this compound maintained at a temperature in the vicinity of the transition. Considerable additional Mössbauer data are given in the following paper. As with all of our Mössbauer spectra, the features in the 163 K spectrum of $[Fe(3\text{-}OCH_3\text{-}SalEen)_2]PF_6$ were least-squares fit to Lorentzian lines, and the areas of the two components of a quadrupole-split doublet were set equal. It is clear that there are only two doublets in this spectrum. One doublet has a quadrupole splitting of 2.928 (5) mm/s and the other 0.52 (4) mm/s. More importantly, the compound which shows the very gradual and incomplete transition (see Figure 1), $[Fe(3\text{-}OCH_3\text{-}SalEen)_2]BPh_4$, also has two quadrupole-split doublets in the 104 K spectrum which is shown as tracing B in Figure 2. It can be seen that the two quadrupole splittings in A and B are essentially the same.

In Figure 3 it is seen that the gradual, but complete, spin-crossover complex $[Fe(SalEen)_2]PF_6$ also shows only two doublets at 158 K with splittings of 2.87 (1) and 0.44 (30) mm/s. At a temperature of ca. 77 K, $[Fe(SalEen)_2]NO_3$ has reached a μ_{eff}/Fe vs. temperature plateau of ca. 3.3 μ_B. In Figure 4 it is seen that only two doublets are seen, one for the molecules that are in the low-spin state and one for those that are in the high-spin state. In no case was there any evidence

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(33) Benson, T. H.; Bilton, M. S.; Gill, N. S. *Aust. J. Chem.* **1977**, *30*, 261.

(34) Supplementary material.

Table XII. Iron-57 Mössbauer Fitting Parameters

compd	T, K[b]	δ, mm s^{-1} [a,b]	ΔE_Q, mm s^{-1} [b]	Γ, mm s^{-1} [b,c]	% area
$[Fe(SalEen)_2]PF_6$	293 (2)	+0.38 (4)	0.40 (10)	0.71 (18), 0.59 (5)	100[d]
	158 (2)	+0.32 (1)	0.44 (30)	0.68 (16), 0.78 (28)	46.6 (3.2)
		+0.215 (4)	2.87 (1)	0.23 (1), 0.18 (1)	53.4 (3.6)
$[Fe(SalEen)_2]NO_3$[g]	293 (2)	+0.372 (4)	0.837 (6)	0.46 (2), 0.39 (1)	100[d]
	163 (2)	+0.39 (1)	0.58 (2)	0.27 (1), 0.37 (2)	26.0 (2)
		+0.235 (1)	2.724 (2)	0.165 (2), 0.172 (2)	74.0 (6)
	84 (3)	+0.39 (1)	0.64 (3)	0.31 (3), 0.38 (4)	18.6 (18)
		+0.243 (1)	2.726 (3)	0.182 (3), 0.179 (3)	81.4 (8)
$[Fe(3\text{-}OCH_3\text{-}SalEen)_2]NO_3$	100.5 (1.0)	+0.231 (1)	2.923 (2)	0.169 (2), 0.148 (2)	100[e]
$[Fe(3\text{-}OCH_3SalEen)_2]BPh_4$	104 (0.5)	+0.48 (6)	0.56 (10)	0.45 (14), 0.46 (17)	10.6 (2)
		+0.25 (1)	2.92 (2)	0.64 (2), 0.26 (1)	89.4 (2)
$[Fe(3\text{-}OCH_3\text{-}SalEen)_2]PF_6$[f]	163.5 (0.7)	+0.45 (2)	0.52 (4)	0.47 (4), 0.53 (5)	43.8 (9)
		+0.226 (3)	2.928 (5)	0.223 (6), 0.174 (5)	56.2 (1.2)

[a] Isomer shifts relative to Fe metal. [b] Error in last significant figure given in parentheses. [c] Half-width at half-maximum listed in order of increasing velocity of the peak. [d] No low-spin signal is readily evident in the spectrum in spite of the fact that the magnetic susceptibility data points to the presence of low-spin complexes. [e] No high-spin signal is readily evident. [f] Considerably more Mössbauer data for this compound are given in the following paper. [g] Preparation 1.

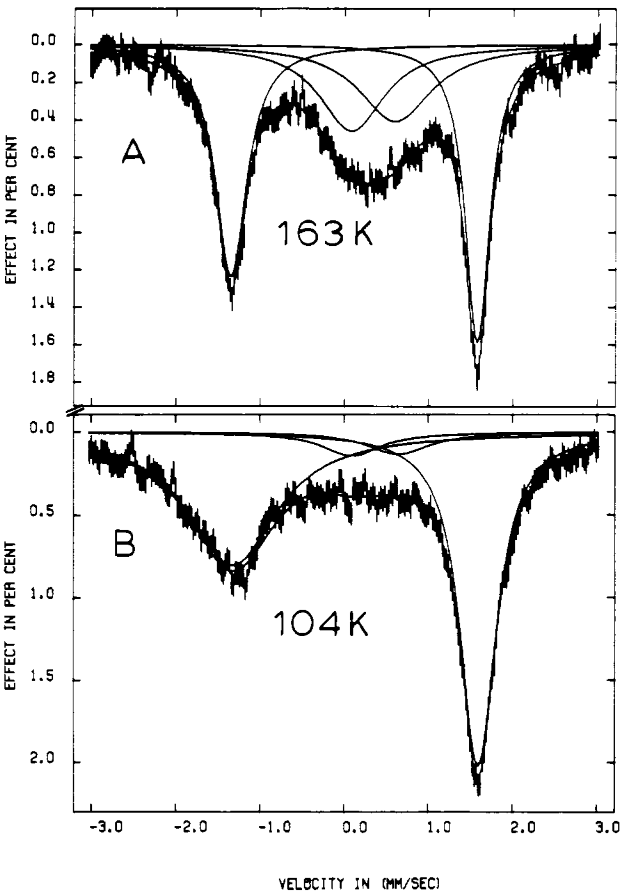

Figure 2. Iron-57 Mössbauer spectra of $[Fe(3\text{-}OCH_3\text{-}SalEen)_2]PF_6$ (A) and $[Fe(3\text{-}OCH_3\text{-}SalEen)_2]BPh_4$ (B). The sample temperatures are indicated.

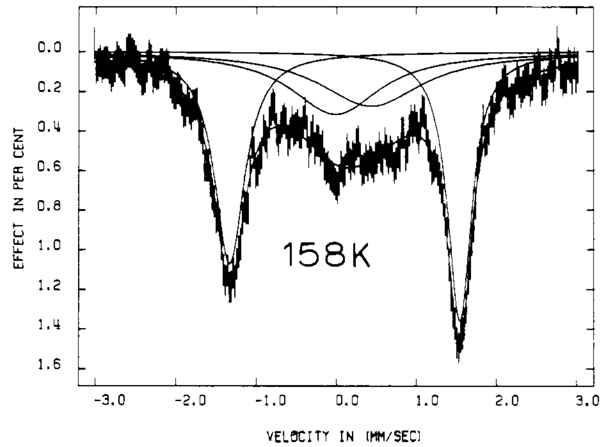

Figure 3. ^{57}Fe Mössbauer spectrum of $[Fe(SalEen)_2]PF_6$ at 158 K.

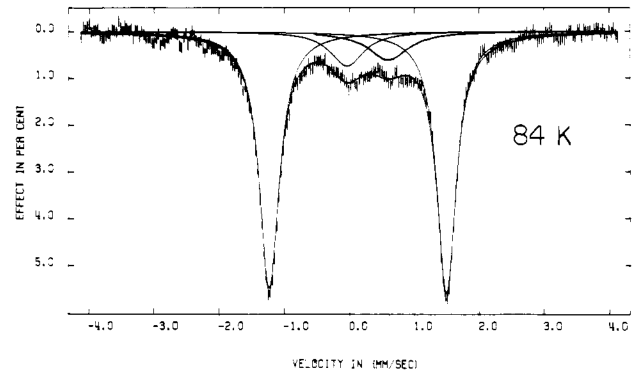

Figure 4. ^{57}Fe Mössbauer spectrum of $[Fe(SalEen)_2]NO_3$, preparation 1, at 84 K.

of a doublet which could be attributed to molecules in an intermediate-spin $^4T_{1g}$ state. A quartet ground state was suggested for one spin-crossover ferric dithiocarbamate complex.[13] For the $[Fe(X\text{-}SalEen)_2]Y$ compounds, the range of quadrupole splitting observed for the low-spin molecules is ca. 2.7–2.9 mm/s and the high-spin range is ca. 0.3–0.85 mm/s. It is to be noted that the range of low-spin quadrupole splittings exceeds the maximum predicted ΔE_Q value that would result from only the valence electrons.[35] However, a similar ΔE_Q range has been observed for the low-spin state in the spin-crossover ferric compounds with thiosemicarbazones of salicylaldehydes or pyruvic acid as ligands.[36] The low-spin compound $[Fe(Saen)_2]Cl\cdot H_2O$, which is different from the SalEen compounds only in not having an ethyl group substituted on the amine nitrogen, exhibits a doublet with $\Delta E_Q = 2.75$ mm/s.[31] In the case of other low-spin Schiff-base ferric complexes, particularly the bis[(*N*-methylethylenediamine)-salicylaldiminato]iron(III) complexes,[11] the ΔE_Q values are of the same magnitude.

The second important observation that can be made from the Mössbauer data for the $[Fe(X\text{-}SalEen)_2]Y$ compounds is that the ratio of the number of high-spin to low-spin molecules,

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as deduced from the areas found for the doublets in the spectra, is less than the ratio calculated from the susceptibility data. Mössbauer spectral areas are given in Table XII. For example, from the 104 K spectrum of [Fe(3-OCH_3-SalEen)$_2$]BPh_4 illustrated in Figure 2, it is found that the high-spin signal area is 10.6% of the total spectral area, while the relative amount of high-spin molecules is calculated to be 89% from the susceptibility data. It is apparent that the Debye–Waller factor which determines the recoilless fraction is less for the high-spin molecules than for the low-spin molecules. This has been observed before.[17,37,38] In other words, the Fe–ligand bonds are stronger in the low-spin molecules, and this leads to a larger recoilless fraction for the low-spin molecules. Not only does the inequality of Debye–Waller factors for the two states make it difficult to assess relative amounts of high-spin and low-spin molecules but also the Lorentzians assigned to the high-spin molecules are found to be very broad. In Table XII it is seen, for example, that the room-temperature spectra for [Fe(SalEen)$_2$]PF_6 and [Fe(SalEen)$_2$]NO_3 appear to show only a single broad signal. The high-spin doublet is so broad that the doublet for the low-spin molecules cannot be resolved. It is only possible to computer fit the single broad features to one doublet, in spite of the fact the magnetic susceptibility data clearly indicate the presence of some low-spin molecules. It must be emphasized that Mössbauer data have been collected for the same samples that were studied with magnetic susceptibility.

The fact that distinct signals are seen for many of the complexes (at least at temperatures lower than room) means that the rate at which individual molecules interchange from high spin to low spin (or vice versa) is less than the inverse of the ^{57}Fe Mössbauer time scale. This third observation translates to a rate of spin flipping less than ca. 10^7 s^{-1}. Apparently the tris(dithiocarbamates) and their selenium analogues are the only ferric spin-crossover complexes which give Mössbauer spectra wherein distinct high-spin and low-spin signals are not seen, but rather one average signal is seen that is the result of spin flipping faster than the inverse of the ^{57}Fe Mössbauer time scale.[39] At present, there is only a single brief report of a spin-crossover complex that has a spin-flipping rate on the order of the reciprocal Mössbauer time scale.[40]

The fourth piece of information available from the Mössbauer spectra comes from the asymmetry seen in the low-spin signals. Figure 5 shows that the two components of the quadrupole-split low-spin doublet have different line widths for the three [Fe(3-OCH_3-SalEen)$_2$]Y compounds. Furthermore, the asymmetry depends upon the counterion Y^-. Examination of Figure 5 shows that the asymmetry is least pronounced in the case of the NO_3^- salt. There is greater asymmetry present in the spectrum of the PF_6^- salt, and, finally, the asymmetry is greatest in the spectrum for the BPh_4^- salt. In a given low-spin doublet, the negative velocity component is always broader than the other component. The asymmetry could be due to the fact that microcrystalline samples were examined; however, we obtained the same spectra for ground samples (see the following paper). There is no appreciable temperature dependence in the asymmetry of a given signal, and the components are of equal area which rules out the Gol'danskii–Karyagin effect.[41]

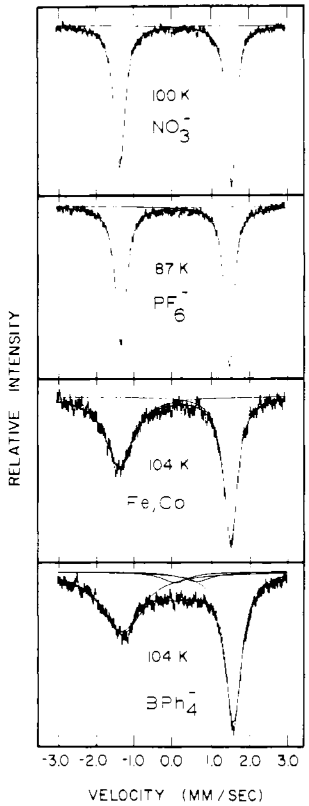

Figure 5. Iron-57 Mössbauer spectra for the compounds [Fe(3-OCH_3-SalEen)$_2$]Y, where Y is NO_3^-, PF_6^-, or BPh_4^-. The spectrum of the doped compound [$Fe_{0.3}Co_{0.7}$(3-OCH_3-SalEen)$_2$]PF_6 is also shown. Sample temperatures are indicated.

A variation in spin-spin relaxation in the compounds is the cause of the variation in asymmetry of the low-spin doublet. The single unpaired electron of a low-spin molecule produces a large local magnetic field, and, depending on the efficiency of the spin–spin relaxation present, the fluctuation frequency of the local magnetic field could be slow, intermediate, or fast relative to the relaxation of the $m_I = \pm^1/_2$ and $\pm^3/_2$ components of the $I = {}^3/_2$ nuclear excited state. For an intermediate frequency of fluctuation of the hyperfine magnetic field, it is expected[42] that the $\pm^1/_2 \rightarrow \pm^3/_2$ component would be broadened more than the $\pm^1/_2 \rightarrow \pm^1/_2$ component. It is clear that spin–spin relaxation is dominant in the [Fe(3-OCH_3-SalEen)$_2$]Y series, because the asymmetry in the low-spin doublet reflects the size of the anion. The larger the anion is, the greater is the asymmetry. Thus, as the *inter*molecular Fe–Fe distance increases, the asymmetry increases. This was further tested by doping one iron compound into a diamagnetic isostructural (see the following paper) host to give [$Fe_{0.3}Co_{0.7}$(3-OCH_3-SalEen)$_2$]PF_6. The ^{57}Fe Mössbauer spectrum for this compound examined at 104 K is shown in Figure 5, where a very asymmetric low-spin doublet is seen. Spin–spin relaxation is dipolar in nature, and therefore it is attenuated with an increase in *inter*molecular Fe–Fe distance.

Since we have demonstrated that the asymmetry in the low-spin doublet is due to spin–spin relaxation and since the broad component is found at negative velocity, it can be concluded that the principal electric field gradient $V_{zz} < 0$. The relatively large ΔE_Q values observed for the [Fe(X-SalEen)$_2$]Y compounds, taken together with the fact that $V_{zz} < 0$, clearly indicate that the ground-state Kramers doublet for these complexes is the doublet where the unpaired electron is in the d_{xy} orbital. This same conclusion was obtained with

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(40) Preliminary results were presented by W. D. Federer, M. S. Haddad, M. W. Lynch, and D. N. Hendrickson at the Symposium on Recent Chemical Applications of Mössbauer Spectroscopy, 179th National Meeting of the American Chemical Society, Houston, March 24–28, 1980; see Abstracts, No. 74. This work will be described in detail in a forthcoming paper.

(41) Greenwood, N. N.; Gibb, T. C. "Mössbauer Spectroscopy"; Chapman and Hall: London, 1971; pp 74–76 and references therein.

(42) (a) Blume, M. *Phys. Rev. Lett.* **1965**, *14*, 96. (b) Wickman, H. H.; Trozzolo, A. M. *Ibid.* **1965**, *15*, 156.

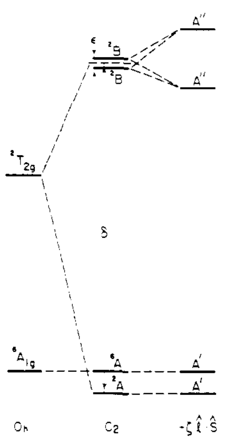

Figure 6. Energy level diagram for the ferric ion $^6A_1$ and $^2T_2$ states in the presence of a rhombic distortion and spin–orbit coupling. C_2 symmetry is appropriate for a meridional isomeric structure for the [Fe(X-SalEen)$_2$]Y complexes.

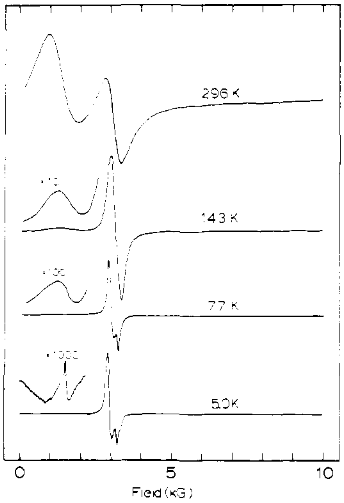

Figure 7. Temperature profile of the X-band EPR spectrum of a microcrystalline sample of [Fe(SalEen)$_2$]PF$_6$.

similar evidence for [Fe(dgm)$_2$(A)]BPh$_4$,[43] where dgm is the dimethylglyoximato anion and A is either imidazole or *N*-ethylimidazole, and for low-spin bis(2,2′,2″-terpyridine)iron(III) perchlorate.[44] The latter compound has a ΔE_Q value of 3.3 mm/s.

Electron Paramagnetic Resonance. EPR can potentially be of use in the study of spin-crossover iron(III) complexes. Important information about the electronic states involved in the transition can be secured if the spin–lattice relaxation is not so severe as to make it difficult to obtain signals. In the case of the spin-crossover ferric dithiocarbamates, EPR signals were difficult to obtain and could only be effectively recorded at liquid-helium temperatures.[8]

Figure 6 gives the energy level diagram for a spin-crossover iron(III) complex. In octahedral symmetry there are two electronic states: $^2T_{2g}$ and $^6A_{1g}$. The combined effects of molecular distortion (illustrated for a rhombic distortion to C_2 symmetry) and spin-orbit interaction splits the $^2T_{2g}$ state into three Kramers doublets which could be energetically well separated. The high-spin $^6A_{1g}$ state is also split into three Kramers doublets, but the splittings between these three doublets are very small (i.e., less than 10 cm^{-1}).

The ^{57}Fe Mössbauer data for the [Fe(X-SalEen)$_2$]Y complexes indicated that only "two" electronic states are thermally populated up to 286 K. These "two" states are the lowest energy Kramers doublet from the low-spin $^2T_{2g}$ state and the array of three Kramers doublets from the $^6A_{1g}$ state. Figure 7 shows variable-temperature EPR data for a microcrystalline sample of [Fe(SalEen)$_2$]PF$_6$ that substantiate this conclusion. This compound undergoes a gradual and essentially complete spin-crossover transition (see Figure 1). At 296 K, two EPR signals are seen, one at g = ca. 4.6 and the other at g = ca. 2.0. As the temperature is decreased, the g = 2.0 signal increases in intensity relative to the g = 4.6 signal until at 5.0 K the g = 4.6 signal is barely observable. The fact that we are able to readily detect EPR signals for both the high-spin and low-spin molecules in these complexes is testimony to the fact that the two excited-state Kramers doublets arising from the $^2T_{2g}$ state are separated from the ground-state Kramers doublet by energies that greatly exceed thermal energies (ca. 200 cm^{-1}) at room temperature. Otherwise, an effective spin-lattice relaxation would be operative.

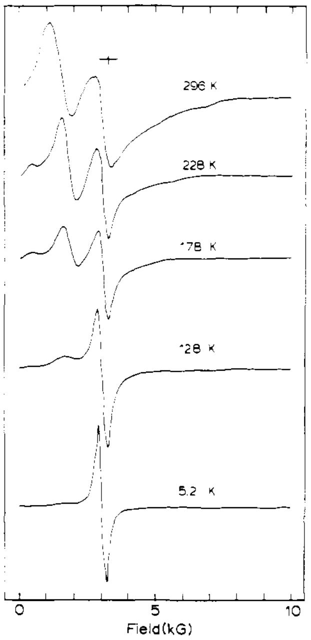

Figure 8. Temperature profile of the X-band EPR spectrum of a microcystalline sample of [Fe(SalEen)$_2$]NO$_3$, preparation 1.

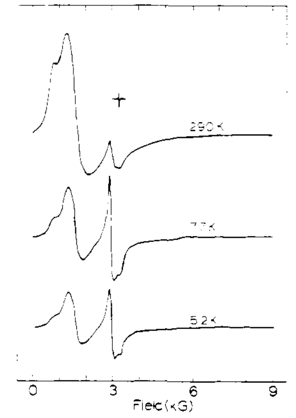

Figure 9. Temperature profiles of the X-band EPR spectrum of a microcrystalline sample of [Fe(3-OCH$_3$-SalEen)$_2$]BPh$_4$.

EPR spectra were also run for compounds that exhibit plateaus in their μ_{eff}/Fe vs. temperature curves and for the one compound that exhibits a sudden and complete transition. Figures 8 and 9 illustrate the variable-temperature EPR spectra obtained for the two plateau compounds [Fe(SalEen)$_2$]NO$_3$ and [Fe(3-OCH$_3$-SalEen)$_2$]BPh$_4$. In each case, two different EPR signals are seen, and as the sample is cooled,

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Table XIII. Experimental and Calculated EPR Parameters

	g(obsd)			g(calcd)								
compd	x	y	z	x	y	z	A	B	C	k	ϵ/ζ	δ/ζ
$[Fe(3\text{-}OCH_3\text{-}SalEen)_2]NO_3\cdot{}^1/_2H_2O$	2.227	2.193	1.939	−2.227	−2.193	+1.939	0.104	0.995	−0.006	0.79	−0.16	7.13
$[Fe(3\text{-}OCH_3\text{-}SalEen)_2]PF_6$	2.220	2.187	1.946	−2.219	−2.187	+1.935	0.109	0.994	−0.007	0.74	−0.15	6.84
$[Fe(3\text{-}OCH_3\text{-}SalEen)_2]BPh_4$	2.203	2.203	1.964	−2.202	−2.202	+1.958	0.085	0.996	0.000	0.90	−0.00	8.71
$[Fe(5\text{-}OCH_3\text{-}SalEen)_2]NO_3$	2.198	2.132	2.020	−2.191	−2.126	+1.977	0.040	0.999	−0.008	0.95	−0.76	11.4
$[Fe(5\text{-}OCH_3\text{-}SalEen)_2](PF_6)_{0.5}(NO_3)_{0.5}$	2.198	2.121	2.027	−2.191	−2.115	+1.979	0.060	0.998	−0.013	0.95	−0.98	11.6
$[Fe(SalEen)_2]NO_3$	2.098	2.098	2.098	*a*	*a*	*a*	*a*	*a*	*a*	*a*	*a*	*a*
$[Fe(SalEen)_2]PF_6$	2.177	2.177	2.015	−2.170	−2.170	+1.974	0.067	0.998	0.000	0.95	0.00	11.0
$[Fe(Saen)_2]Cl\cdot H_2O$	2.213	2.146	2.005	−2.207	−2.141	+1.972	0.068	0.998	−0.011	0.95	−0.63	10.4

[a] Not calculated because isotropic $g > 2$.

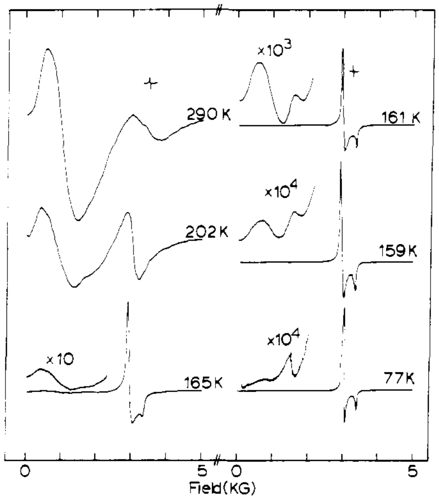

Figure 10. Temperature profile of the X-band EPR spectrum of $[Fe(3\text{-}OCH_3\text{-}SalEen)_2]PF_6$.

the g = ca. 2.0 signal grows at the expense of the g = ca. 4.2 signal. The former compound plateaus at a value of μ_{eff}/Fe = 3.26 μ_B and a weak high-spin g = ca. 4.2 signal is still clearly visible for this compound even at 5.2 K. The compound $[Fe(3\text{-}OCH_3\text{-}SalEen)_2]BPh_4$ plateaus at a considerably higher value of μ_{eff}/Fe, and, in keeping with this, the 5.2 K EPR spectrum in Figure 9 shows comparable intensity in the g = ca. 4.2 and g = 2.0 signals.

The sudden spin-crossover complex $[Fe(3\text{-}OCH_3\text{-}SalEen)_2]PF_6$ gives very interesting EPR data, as illustrated in Figure 10. It is seen that, in agreement with the magnetic susceptibility data, there is a dramatic change in the EPR spectrum occurring within a range of a few degrees at ca. 160 K. In addition, another unusual occurrence is noted in the EPR spectrum for this compound. The high-spin EPR signal is found at a considerably lower magnetic field than the corresponding signals for the other compounds. An effective g value of 7.5 is calculated from the low-field derivative in the 290 K spectrum (midpoint field position between two turning points). This signal disappears at low temperatures to show a very weak signal at g = ca. 4.3 (see the 77 K spectrum). For simple high-spin low-symmetry ferric complexes an intense signal around g = ca. 4.3 is usually observed. This EPR resonance arises from transitions within the $M_s = \pm{}^3/_2$ high-spin Kramers doublet. The zero-field splitting in the high-spin state is gauged by $\hat{H} = D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2)$, where D and E are the axial and rhombic zero-field splitting parameters, respectively. The presence of a strong g = ca. 4.3 signal indicates[45-48] that the molecular symmetry is low (rhombic) and $E/D \approx {}^1/_3$ and $h\nu/D \leq 3$, where $h\nu$ is the microwave energy (ca. 0.3 cm^{-1} at X-band frequencies). An $M_s = \pm{}^3/_2$ signal at higher g values (e.g., g = 6.0) will be seen when the complex is axial as reflected by $E \approx 0$. It is clear that the high-spin molecules in the sudden transition compound $[Fe(3\text{-}OCH_3\text{-}SalEen)_2]PF_6$ are experiencing a molecular distortion that is different than that which dominates in the other compounds. It is possible that they are distorted into a more axial form by lattice energies, and this distortion is relieved suddenly at ca. 160 K.

At low temperatures the EPR signal seen at g = ca. 2 for the ground-state Kramers doublet is well resolved. Table XIII gives the g values for the various compounds. It is possible to use these g value patterns to elucidate the nature of the ground-state Kramers doublet.[45,49] If the appropriate one-electron orbitals for the $t_{2g}{}^5$ configuration are employed with the Hamiltonian

$$\hat{H} = \zeta\hat{l}\cdot\hat{s} - \delta(\hat{l}_z^2 - {}^2/_3) - (\epsilon/2)(\hat{l}_+^2 + \hat{l}_-^2)$$

then a set of three secular equations results for the ground-state Kramers doublet. In the above Hamiltonian operator, ζ is the one-electron spin–orbit coupling constant, δ is the one-electron parameter gauging an axial distortion, and ϵ gauges any lower symmetry distortion. The secular equations can be solved to give wavefunctions upon which application of a Zeeman Hamiltonian operator gives

$$g_z = -2[A^2 - B^2 + C^2 + k(A^2 - C^2)]$$
$$g_x = 2[2AC - B^2 + kB(2^{1/2})(C - A)]$$
$$g_y = -2[2AC + B^2 + kB(2^{1/2})(C + A)]$$

In the above expressions for the components of the **g** tensor, k is the orbital reduction factor and the parameters A, B, and C are used to characterize the two spinors of the ground-state Kramers doublets:

$$\psi = A|+1^+\rangle + B|\zeta^-\rangle + C|-1^+\rangle$$
$$\psi' = A|-1^-\rangle - B|\zeta^+\rangle + C|+1^-\rangle$$

where

$$\zeta = (1/2^{1/2})[|2\rangle - |-2\rangle]$$

A computer program was written to least-squares fit the observed g values for a compound to the above g-value equations and the normalization condition ($A^2 + B^2 + C^2 = 1$) to give values of A, B, C, and k. The values of these four fitting parameters are collected in Table XIII. In each case, values for δ and ϵ can be calculated from the fitting parameters. In the absence of the knowledge of the sign of the observed g

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values and their assignments, it was necessary to try many assignments for each compound. The best fits were selected on the basis of physically reasonable values of k, δ, and ϵ.

Perusal of Table XIII shows that in all cases the value of B is very large which indicates that the ground-state Kramers doublet consists mainly of a state wherein the unpaired electron resides in the d_{xy} orbital. This is in agreement with our interpretation of the Mössbauer data. Another important result is that δ/ζ ranges between 6.8 and ca. 11.6. If the free-ion one-electron spin–orbit constant is taken as 460 cm^{-1}, δ ranges between 1500 and 4800 cm^{-1}. In other words, the energy difference between the ground-state Kramers doublet A′ and the center of gravity of the two excited doublets (both A″) from the low-spin manifold is very large. This explains why it is easy to see EPR spectra even at room temperature, for it has been shown that the rate of spin–lattice relaxation ($1/T_1$) is proportional to $(\zeta^2H_0{}^4T)/\delta^4$, where H_0 is the magnetic field.[46]

Conclusion

The series of compounds [Fe(X-SalEen)$_2$]Y has been shown to exhibit most all of the curiosities observed for spin-crossover complexes in the solid state. It is shown with EPR and ^{57}Fe Mössbauer data that regardless of the shape of the μ_{eff}/Fe vs. temperature curve only two states, the high-spin $^6A_{1g}$ and the lowest energy Kramers doublet from $^2T_{2g}$, are thermally populated for these compounds. There is no evidence for population of an intermediate-spin ($^4T_{1g}$) state. The ground-state Kramers doublet has been characterized as d_{xy}.

Acknowledgment. The support of the National Institutes of Health under Grant HL13652 is gratefully acknowledged. Thanks are in order to Professor Peter Debrunner for the use of his Mössbauer instrumentation.

Note Added in Proof. A low-temperature ^{57}Fe Mössbauer spectrum was run for a sample of the essentially low-spin compound [Fe(3-OCH$_3$-SalEen)$_2$]NO$_3$·$^1/_2$H$_2$O in the presence of a large (ca. 60 kG) longitudinal applied magnetic field. The appearance of a "doublet–triplet" pattern with the triplet at more positive velocities corroborates the conclusion reached in this work that $V_{zz} < 0$ for the the low-spin [Fe(X-SalEen)$_2$]Y complexes. This conclusion was reached previously on the basis of the asymmetry of the quadrupole doublets at zero applied field.

Registry No. [Fe(SalEen)$_2$]PF$_6$, 73261-28-6; [Fe(SalEen)$_2$]NO$_3$, 73370-18-0; [Fe(3-OCH$_3$-SalEen)$_2$]NO$_3$, 75112-21-9; [Fe(3-OCH$_3$-SalEen)$_2$]BPh$_4$, 73261-30-0; [Fe(3-OCH$_3$-SalEen)$_2$]PF$_6$, 73261-31-1; [Fe(5-OCH$_3$-SalEen)$_2$]NO$_3$, 75112-23-1; [Fe(5-OCH$_3$-SalEen)$_2$](PF$_6$)$_{0.5}$(NO$_3$)$_{0.5}$, 75112-24-2; [Fe(Saen)$_2$]Cl, 75112-25-3; [Fe(5-OCH$_3$-SalEen)$_2$]BPh$_4$, 75112-26-4; [Co(3-OCH$_3$-SalEen)$_2$]PF$_6$, 75083-22-6; [Fe(SalEen)$_2$]BPh$_4$, 75112-27-5; salicylaldehyde, 90-02-8; 5-methoxysalicylaldehyde, 672-13-9; *N*-ethylethylenediamine, 110-72-5; ethylenediamine, 107-15-3; 3-methoxysalicylaldehyde, 148-53-8.

Supplementary Material Available: Tables I–XI, magnetic susceptibility data (14 pages). Ordering information is given on any current masthead page.

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Spin-Crossover Ferric Complexes: Unusual Effects of Grinding and Doping Solids

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Magnetic Susceptibility, EPR, ^{57}Fe Mössbauer, and X-ray powder diffraction data are presented for the [Fe(X-SalEen)$_2$]Y series of ferric spin-crossover complexes to substantiate the presence of the nucleation and growth mechanism for the spin-crossover phase transition in solid samples of these complexes. The compound [Fe(3-OCH$_3$-SalEen)$_2$]PF$_6$, where 3-OCH$_3$-SalEen is the monoanion of the Schiff-base condensation product from 3-methoxysalicylaldehyde and *N*-ethylethylenediamine, exhibits an almost discontinuous spin-crossover transition with a hysteresis of 2–4°. Grinding a microcrystalline sample of this compound leads to an incompleteness of the transition; some complexes persist in the high-spin state at low temperatures. The transition also becomes more gradual upon sample grinding, and more low-spin molecules form in the ground samples at higher temperatures compared to the unground samples. The temperature at which there are equal numbers of low-spin and high-spin molecules also shifts to a lower value upon sample grinding. The effects of sample grinding are found to be general for the [Fe(X-SalEen)$_2$]Y complexes and are most likely attributable to defects caused by the grinding. Physical data point to the presence of molecules in only two electronic states even for the ground samples. The results of a study of crystalline doped [Fe$_x$Cr$_{1-x}$(3-OCH$_3$-SalEen)$_2$]PF$_6$ and [Fe$_x$Co$_{1-x}$(3-OCH$_3$-SalEen)$_2$]PF$_6$ show that the effects of doping (e.g., more gradual transition) are very similar to those seen for sample grinding. In fact, grinding a doped sample leads to the most pronounced change. For the doped samples it is found on one hand that, as the chromium(III) concentration is increased, the transition temperature shifts to lower temperature, whereas on the other hand, as the cobalt(III) concentration is increased, there is a shift to higher temperature. An explanation of the various observations in terms of the nucleation and growth mechanism of phase transitions in the solid state is given. The results of some interesting EPR observations on these ground and doped [Fe(X-SalEen)$_2$]Y complexes are reported.

Introduction

In the preceding paper, variable-temperature magnetic susceptibility, EPR, and ^{57}Fe Mössbauer results were presented for the [Fe(X-SalEen)$_2$]Y series of ferric spin-crossover complexes. It was shown that the full range of unusual phenomena is seen for these spin-crossover complexes in the solid state. The temperature dependence of the magnetic susceptibility for a compound does not simply reflect a Boltzmann distribution over thermally populated states. In the case of many compounds, the spin-crossover transformation does not go to completion as the sample temperature is decreased. Different preparations of a given complex exhibit appreciable differences in physical properties. No evidence of an intermediate-spin state was found.

It is our hypothesis that all of the curiosities observed for the spin-crossover complexes in the solid state can be explained by the general nucleation and growth mechanism of phase transitions in solids.[3,4] The spin-crossover transformation is

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