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Synthesis and Spin-State Studies in Solution of γ-Substituted Tris(β-diketonato)iron(III) Complexes and Their Spin-Equilibrium β-Ketoimine Analogues Derived from Triethylenetetramine[1]

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Six tris(β-diketonato)iron(III) complexes, viz., [Fe(acacX)$_3$], and eight new magnetically anomalous β-ketoimineiron(III) complexes containing hexadentate ligands derived from triethylenetetramine (trien) and various β-diketones ([Fe((acac)$_2$trien)](Y) from acetylacetone with Y^- = PF_6^-, BPh_4^-, Br^-, and I^-, [Fe((bzac)$_2$trien)](PF$_6$) and [Fe((bzacCl)$_2$trien)](PF$_6$) from benzoylacetone, and [Fe((tfac)$_2$trien)](PF$_6$) from trifluoroacetylacetone) have been synthesized and studied. The tris chelates have been synthesized by new or modified methods, in most cases from the parent [Fe(acac)$_3$] complex, and are found to exist as typical pseudooctahedral high-spin ($S = {}^5/_2$) iron(III) complexes. On the basis of a radical-trap experiment, the chlorination of [Fe(acac)$_3$] by *N*-chlorosuccinimide (NCS) to form [Fe(acacCl)$_3$] is postulated to undergo an *ionic* (Cl^+) intermediate. In *solution*, the β-ketoimine complexes are hexacoordinate, uni-univalent electrolytes which exhibit variable-temperature magnetic susceptibility data and electronic spectra which are consistent, in six cases, with a ${}^2T \rightleftarrows {}^6A$ spin-equilibrium process arising from iron(III) in a tetragonally distorted N_4O_2 ligand field environment like that found for the previously studied [Fe((XSal)$_2$trien)](Y) series (Sal = salicylaldehyde). Two of the complexes, [Fe((acacCl)$_2$trien)](PF$_6$) and [Fe((bzacCl)$_2$trien)](PF$_6$), have been synthesized by direct chlorination of the β-ketoimine rings of [Fe((acac)$_2$trien)](PF$_6$) and [Fe((bzac)$_2$trien)](PF$_6$) using NCS in a manner similar to that used for the preparation of [Fe(acacCl)$_3$]. The two chlorinated β-ketoimine complexes are found to favor the low-spin electronic state over that of their parent complexes, suggesting that the spin state is dependent on the electron-withdrawing capability of the chelate ring substituent. The ${}^2T \rightleftarrows {}^6A$ spin equilibrium for the parent [Fe((acac)$_2$trien)](Y) complex is strongly solvent dependent and exhibits an anion dependence which is surprisingly large in comparison with that of [Fe(Sal$_2$trien)](Y). The solvent dependency on the magnetic moment cannot be completely attributable to a secondary amine [N–H···solvent] hydrogen-bonding interaction involving the trien backbone as previously noted for the [Fe(Sal$_2$trien)]$^+$ complex. Laser Raman temperature-jump kinetic measurements, conducted in collaboration with Dr. Norman Sutin, yield spin-state lifetimes for the [Fe((acac)$_2$trien)](PF$_6$) salt in a methanol/10% acetone solution of $\tau({}^2T) = 6.7 \times 10^{-8}$ s and $\tau({}^6A) = 1.5 \times 10^{-7}$ s at 298 K which are similar in magnitude to those previously reported for other iron $\Delta S = 2$ spin-equilibrium processes. The room-temperature Mössbauer spectrum of the ${}^2T \rightleftarrows {}^6A$ [Fe((acac)$_2$trien)](BPh$_4$) complex ($\mu_{\text{eff}} = 3.04\ \mu_B$) shows separate signals attributable to the ${}^6A$ and ${}^2T$ spin states, indicating that $\tau({}^2T)$ and $\tau({}^6A)$ in the solid state for a dynamic spin-equilibrium process are $>10^{-7}$ s.

Introduction

Transition metal chelates exhibiting a "spin equilibrium" between thermally populated low-spin (ls) and high-spin (hs) electronic states have been much studied over the last 40 years since the phenomenon was first observed for the tris(dithiocarbamato)iron(III) complexes.[4] Essentially all of these investigations, however, have been confined to the solid state,[5,6] with variable-temperature magnetochemistry and Mössbauer spectroscopy (for iron systems) being used to study the anomalous magnetic properties of such variable-spin compounds in their spin-crossover regions. Recently, we have initiated efforts to extend systematically the study of variable-spin systems into the *solution* state[7–10] where (1) variable-temperature magnetic properties are not obscured by unpredictable lattice effects such as phase changes, hysteresis, or *inter*molecular metal–metal magnetic exchange interactions, (2) the kinetics of the dynamic *intra*molecular ls $\rightleftarrows$ hs spin-interconversion (intersystem crossing) processes can be measured, and (3) the role and energetics of spin-multiplicity changes on electron-transfer processes of both inorganic and some metalloprotein reactions can be directly probed.

In the present work, we report the solution-state properties of a new Fe(III) spin-equilibrium system derived from triethylenetetramine (trien) and various β-diketones to produce the hexadentate β-ketoimine ligands shown in Figure 1. Six-coordinate cobalt(III) and nickel(II) complexes containing some of these ligands have been reported by other workers,[11] but their chemistry with iron has been completely neglected. In solution, variable-temperature magnetic and electronic spectral data have characterized three of the new β-ketoimine iron(III) compounds (R = CH_3, X = H; R = CH_3, X = Cl; R = Ph, X = H) as possessing ${}^2T$(ls, $S = {}^1/_2$) $\rightleftarrows$ ${}^6A$(hs, $S = {}^5/_2$) spin-equilibrium centers in tetragonally distorted ligand field environments with N_4O_2 donor atom sets. Thus, these complexes, along with the previously reported and structurally similar [Fe((XSal)$_2$trien)]$^+$ series,[10] are the only known ${}^2T \rightleftarrows {}^6A$ spin-equilibrium compounds to be devoid of Fe–S bonding. The remaining two β-ketoimine derivatives of Figure 1 (R = Ph, X = Cl; R = CF_3, X = H) also appear to exhibit a spin equilibrium between two electronic states, but, as of yet, with an incompletely characterized electronic ground state. In solution, the spin equilibria can be partially "controlled" as desired by predictable solvent and R- and X-group electronic substituent effects. In addition, preliminary data are presented in which dynamic spin-state lifetimes, $\tau({}^2T)$ and $\tau({}^6A)$, for the ${}^2T \rightleftarrows {}^6A$ [Fe((acac)$_2$trien)](PF$_6$) complex have been measured directly by laser Raman temperature-jump kinetics.

Also shown in Figure 1 are a series of high-spin ${}^6A$ X-substituted tris(acetylacetonato)iron(III) complexes which have also been synthesized in this work. All of these compounds have been previously reported,[12–15] but it was found that many of the literature preparations could be improved by some modifications, with these modifications being especially useful in synthesizing the new X = Cl β-ketoimineiron(III) spin-equilibrium complexes. A radical-trap experiment involving the reaction of [Fe(acac)$_3$] with *N*-chlorosuccinimide to produce [Fe(acacCl)$_3$] has indicated that chlorination of the chelated β-diketone ring proceeds to a large extent via electrophilic attack by Cl^+. Furthermore, it is speculated that similar electrophilic substitution reactions on the β-ketoimine rings of the variable-spin Fe(III) complexes might be spin-state dependent. Although unexplored in the present work, it is also possible that the present β-ketoimine complexes, being structurally related to the catalytically active [Fe(acac)$_3$] species,[16] could serve as spin-state-dependent homogeneous catalysts for certain organic reactions.

Experimental Section

Physical Measurements. Magnetic susceptibilities in the solid state were measured at room temperature by the Faraday technique using

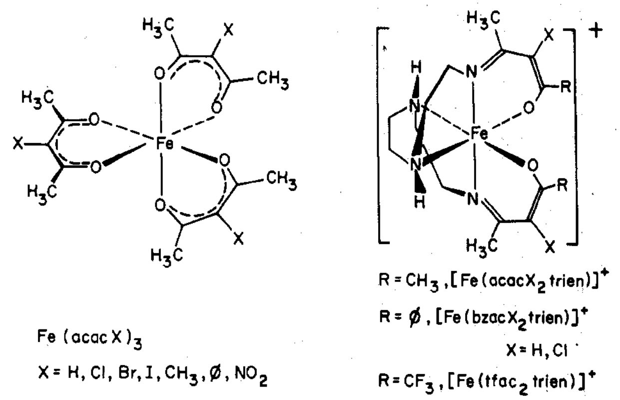


Figure 1. Structure of the pseudooctahedral γ-substituted tris(β-diketonato)iron(III) and β-ketoimineiron(III) complexes.

$Hg[Co(NCS)_4]$ as the calibrant. Pascal constants were used to correct for ligand and anion diamagnetism, in 10^{-6} cgsu: $acac^-$, −52; $acacCl^-$, −65; $acacBr^-$, −76; $acacI^-$, −97; $acacCH_3^-$, −67; $acacPh^-$, −118; $acacNO_2^-$, −58; $(acac)_2trien^{2-}$, −176; $(acacCl)_2trien^{2-}$, −210; $(bzac)_2trien^{2-}$, −226; $(bzacCl)_2trien^{2-}$, −251; $(tfac)_2trien^{2-}$, −196; PF_6^-, −64; BPh_4^-, −220; Br^-, −35; I^-, −50.

Measurements in solution were performed by the Evans ^1H NMR method.[17] A methanol sample was used for temperature calibration. A first-order correction for changes in solvent density and sample concentration with temperature was used.[18] Chloroform, TMS, and *tert*-butyl alcohol were used as reference compounds, the last being used for the D_2O solutions. Solvent and reference compound proton signals were generally found to give identical ^1H NMR splittings and, thus, identical calculated moments. For the 50:50 mole fraction water/acetone solution, the three reference compounds dissolved in the same sample all gave identical ^1H NMR splittings to within experimental error (~2%). Thus, all three reference compounds were judged to be inert in these studies and could be used interchangeably.

Solid- and solution-state infrared spectra were obtained on a Beckman IR-20 using NaCl plates and Nujol mulls for the solids and Beckman IR-Tran2 cells for the solutions. Uv–vis spectra were run on a Cary 17 instrument using jacketed, insulated quartz cells; reported sample temperatures are ±1 °C and were monitored using a thermistor. ^1H NMR spectra for the Evans method were obtained on a Varian A-56/60A spectrometer. Room-temperature Mössbauer spectra were run on an apparatus already described[19] and analyzed using the program of Chrisman and Tumolillo;[20] isomer shifts, δ, are reported in mm s^{-1} relative to a room-temperature sodium nitroprusside spectrum.

Molecular weights in chloroform at 39.5 °C were determined using a Hewlett-Packard 302B vapor pressure osmometer. Solution conductivities in acetone and acetonitrile were obtained with a Model 31 YSI conductivity bridge. Elemental analyses were performed by PCR, Inc., Gainesville, Fla., and by the microanalytical laboratory of the School of Chemical Sciences, University of Illinois.

The temperature-jump experiments were performed using the laser-stimulated Raman system previously described.[21] For the experiments, sample cells with 0.020–0.081-mm path lengths were employed. A methanol/10% acetone solution was used and data were obtained at 25 ± 2 °C in thermostated cells. The relaxation traces obtained from photographs of oscilloscope traces measured the change in optical density of the sample spectrum with time. The first-order relaxation time, τ in ns, for the

$$^2T(Fe^{3+}, ls) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} {}^6A(Fe^{3+}, hs)$$

spin interconversion process was determined from log $(I_\infty - I)$ vs. time plots generated from the photographs. Equilibrium constants, $K_{eq} = k_1/k_{-1}$, were obtained from the magnetic susceptibility measurements, with the value used being 2.26 at 25 °C for the $[Fe((acac)_2trien)](PF_6)$ compound in methanol/10% acetone solution. Rate constants, k_1 and k_{-1}, were calculated from the measured relaxation time of $\tau = 45 \pm 10$ ns at 25 °C and the equilibrium constant, using the relationship, $\tau = (k_1 + k_{-1})^{-1}$. The 10-ns error in τ is estimated from the range of τ values obtained from six different lasing experiments on the same sample. The spin-state lifetimes, $\tau(^2T)$ $\tau(^6A)$, are then simply k_1^{-1} and k_{-1}^{-1}, respectively.

Materials and Syntheses. Technical grade triethylenetetramine (trien) from Aldrich and purified grade LiBr from Fisher were used as received. Trifluoroacetylacetone was purified by vacuum distillation from P_2O_5 before use. All other solvents and reagents used in syntheses were reagent grade. Spectroquality acetone, CH_3OH, and $CHCl_3$ and reagent grade CH_3CN, CH_2Cl_2, THF, DMSO, and nitrobenzene were used for the ir, visible, and ^1H NMR studies.

Reported melting points are corrected. Where more than one mass spectrometric parent ion peak is indicated, the numbers in parentheses are the respective relative intensities.

$[Fe(acacCl)_3]$ was prepared by refluxing a solution of 0.70 g of $[Fe(acac)_3]$ (2 mmol) and 1.35 g of *N*-chlorosuccinimide (10 mmol) in 40 ml of CCl_4 for 3 h. The reaction mixture was cooled to 0 °C for 3 h and filtered. After removal of solvent, the solid substance was recrystallized twice from acetone/water and dried in vacuo over P_2O_5 for 6 h yielding 0.40 g (44%) of red-purple crystals, mp 154 °C (lit.[14] mp 152 °C). Anal. Calcd for $C_{15}H_{18}Cl_3FeO_6$: C, 39.47; H, 3.97; Cl, 23.30; Fe, 12.23. Found: C, 38.96; H, 3.99; Cl, 24.08; Fe, 12.05. Molecular weight: calcd, 456; found, 463 ± 10 by osmometry, M_{P^+} 455, 457 (1:1) by mass spectrometry. There is a broad Mössbauer singlet at $\delta = 0.61$ (0.03) mm s^{-1}; $\mu_{eff,298}$(solid) = 5.89 μ_B.

The synthesis, when repeated in the presence of the radical trap 4-*tert*-butylcatechol (1:1 $[Fe(acac)_3]$ to catechol), yielded the same trichlorinated $[Fe(acacCl)_3]$ complex.

$[Fe(acacBr)_3]$ was prepared in the same manner as that for $[Fe(acacCl)_3]$ and as that described briefly by Collman[12] using *N*-bromosuccinimide (10 mmol) in CCl_4. The solid substance obtained was recrystallized from CH_2Cl_2/acetone and dried in vacuo over P_2O_5 for 6 h, yielding 0.35 g (30%) of dark purple needles, mp 158 °C dec (lit.[14] mp 170 °C). Anal. Calcd for $C_{15}H_{18}Br_3FeO_6$: C, 30.54; H, 3.08; Br, 40.64; Fe, 9.47. Found: C, 31.17; H, 3.19; Br, 39.74; Fe, 9.54. Molecular weight: calcd, 590; found, 612 ± 13 by osmometry, M_{P^+} 587, 589, 591, 593 (1.6, 3.2, 3.8, 1) by mass spectrometry. No Mössbauer data are available since absorption is less than 0.05% at 298 K; $\mu_{eff,298}$(solid) = 5.96 μ_B.

$[Fe(acacI)_3]$ was prepared by synthesis of the ligand by the method of Kumler[22] on a triple scale without drying of the product. A solution of 13.0 g of $FeCl_3 \cdot 6H_2O$ (48 mmol) in 80 ml of H_2O was added to the vigorously stirred ligand. On addition of 350 ml of 0.5 N aqueous NaOAc, the product appeared as dark crystals. (Note: the product is sometimes obtained as an oil which is difficult to crystallize.) The product was collected, washed with 1 l. of H_2O and with 200 ml of ether, and dried in vacuo over P_2O_5 for 14 h and then at 40° for 5 h, yielding 10.0 g (28%) of red-purple crystals, mp 158 °C (lit.[14] mp 156 °C). Anal. Calcd for $C_{15}H_{18}FeI_3O_6$: C, 24.65; H, 2.48; Fe, 7.64; I, 52.09. Found: C, 25.26; H, 2.45; Fe, 6.30; I, 56.84. Molecular weight: calcd, 731; found, 727 ± 15 by osmometry; no M_{P^+} observed in mass spectrum. There is a broad Mössbauer singlet at $\delta = 0.55$ (0.08) mm s^{-1}.

$[Fe(acacCH_3)_3]$ was prepared by addition of 1.37 g of 3-methyl-2,4-pentanedione (12 mmol) to a stirring solution of 1.35 g of $FeCl_3 \cdot 6H_2O$ (5 mmol) in 25 ml of H_2O. After addition of 1.9 g of $NaOAc \cdot 3H_2O$ (13.2 mmol) and 1.5 h of stirring, the solid product was collected and washed with 500 ml of H_2O. Recrystallization from CH_2Cl_2/*n*-hexane and drying in vacuo over P_2O_5 for 6 h yielded 0.90 g (56%) of dark red crystals, mp 188 °C dec. Anal. Calcd for $C_{18}H_{27}FeO_6$: C, 54.70; H, 6.89; Fe, 14.13. Found: C, 54.23; H, 6.76; Fe, 14.24. Molecular weight: calcd, 395. Found, 385 ± 9 by osmometry, M_{P^+} 395 by mass spectrometry. There is a broad Mössbauer singlet at $\delta = 0.68$ (0.02) mm s^{-1}; $\mu_{eff,298}$(solid) = 5.96 μ_B.

$[Fe(acacPh)_3]$ was prepared and recrystallized by the same method as that described above for $[Fe(acacCH_3)_3]$, using 3-phenyl-2,4-pentanedione. Addition of about 8 ml of acetone or methanol aids in solubility of the ligand. This method yields 1.45 g (50%) of red crystals, mp 246 °C dec. Anal. Calcd for $C_{33}H_{33}FeO_6$: C, 68.17; H, 5.72; Fe, 9.60. Found: C, 68.56; H, 5.69; Fe, 9.60. Molecular weight: calcd, 581; found, 577 ± 11 by osmometry, M_{P^+} 581 by mass spectrometry. There is a broad Mössbauer singlet at $\delta = 0.82$ (0.03) mm s^{-1}; $\mu_{eff,298}$(solid) = 6.00 μ_B.

$[Fe(acacNO_2)_3]$ was prepared using a modification of the procedure of Sen and Thankarajan[23] for $[Cr(acacNO_2)_3]$. A 3.2-g sample of $[Fe(acac)_3]$ (9 mmol), 25 ml of acetic anhydride, and 2.2 ml of 16 N HNO_3 (35 mmol) were all cooled separately to 0 °C. The complex was suspended in the acetic anhydride and was stirred vigorously during the *dropwise* addition of the nitric acid. The mixture was stirred at 0 °C for 1 h and then at 25 °C for 1 h. A 100-g sample of ice in 200 ml of 1 N NaOAc was added, and the reaction mixture was stirred for 10 min (until the ice just melts). The crystals were collected and washed with 500 ml of H_2O and then with three 50-ml portions of petroleum ether. Recrystallization from CH_2Cl_2/*n*-heptane and drying in vacuo over P_2O_5 for 48 h yielded 1.57 g (36%) of red-orange crystals, mp 196 °C dec (lit.[15] mp 196 °C). Anal. Calcd for $C_{15}H_{18}FeN_3O_{12}$: C, 36.90; H, 3.72; Fe, 11.44; N, 8.61. Found: C, 37.70; H, 3.85; Fe, 11.26; N, 8.33. Molecular weight: calcd, 488; found, 488 ± 7 by osmometry, M_{P^+} 488 by mass spectrometry. There is a broad Mössbauer singlet at $\delta = 0.60$ (0.04) mm s^{-1}; $\mu_{\mathrm{eff},298}$(solid) = 5.96 μ_B. [*Caution! This reaction mixture of acetic anhydride and concentrated HNO_3 is potentially explosive!*[24]]

[Fe((acac)$_2$trien)](PF$_6$) was prepared by adding 14.5 g of trien (100 mmol) dissolved in 30 ml of methanol to a stirring solution of 25.0 g of 2,4-pentanedione (250 mmol) in 50 ml of methanol. After being stirred for 10 min, the solution turned yellow. To this stirring solution, 13.5 g of $NaOCH_3$ (250 mmol) suspended in 130 ml of methanol was added in eight portions. Finally, 40.4 g of $Fe(NO_3)_3\cdot9H_2O$ (100 mmol) dissolved in 125 ml of methanol was added and the mixture was stirred for 1.5 h. The mixture was filtered to remove excess salts, and the solvent was removed. The solid thus obtained was suspended in 500 ml of H_2O and filtered, removing [Fe(acac)$_3$] which is a by-product of the reaction. To this filtrate was added a solution of 18.6 g of KPF_6 (100 mmol) dissolved in 150 ml of H_2O, and the mixture was stirred for 30 min. The dark red-purple crystals which formed were collected and recrystallized from CH_2Cl_2/CCl_4, yielding 20.25 g (40%); mp 253 °C dec. Anal. Calcd for $C_{16}H_{28}F_6FeN_4O_2P$: C, 37.74; H, 5.54; Fe, 10.97; N, 11.00. Found: C, 38.01; H, 5.61; Fe, 10.63; N, 11.20. $\Lambda_c = 177$ $\mu\Omega^{-1}$ cm^{-1} at 30 °C and 10^{-3} M in acetone. There is a broad Mössbauer singlet at $\delta = 0.52$ (0.02) mm s^{-1}; $\mu_{\mathrm{eff},298}$(solid) = 6.00 μ_B.

[Fe((bzac)$_2$trien)](PF$_6$) was prepared by adding a solution of 6.5 g of benzoylacetone (40 mmol) in 10 ml of methanol to a stirring solution of 2.9 g of trien (20 mmol) in 6 ml of methanol. After 30 min of stirring, 2.2 g of $NaOCH_3$ (40 mmol) was suspended in 20 ml of methanol and added in ten portions, and then a solution of 8.1 g of $Fe(NO_3)_3\cdot9H_2O$ (20 mmol) in 25 ml of methanol was added dropwise. Finally, a solution of 3.7 g of KPF_6 (20 mmol) in 50 ml of methanol was added, and the mixture was stirred for 1.5 h. Filtration, removal of solvent, extraction into acetone, filtration, removal of solvent under reduced pressure, and recrystallization from CH_2Cl_2/CCl_4 yielded 3.1 g (24%) of a red-purple powder, mp >360 °C. Anal. Calcd for $C_{26}H_{32}F_6FeN_4O_2P$: C, 49.30; H, 5.09; Fe, 8.82; N, 8.85. Found: C, 49.33; H, 4.97; Fe, 8.51; N, 8.82. $\Lambda_c = 161$ $\mu\Omega^{-1}$ cm^{-1} at 30 °C and 10^{-3} M in acetone. There is a broad Mössbauer singlet at $\delta = 0.55$ (0.02) mm s^{-1}; $\mu_{\mathrm{eff},298}$(solid) = 5.89 μ_B.

[Fe((tfac)$_2$trien)](PF$_6$) was prepared in the same manner as that for [Fe((acac)$_2$trien)](PF$_6$), but on a 2.6-mmol scale. Recrystallization was accomplished with CH_2Cl_2 and the slightly hygroscopic solid material was dried in vacuo over P_2O_5 at 25 °C for 24 h and then at 117 °C for an additional 24 h. The product, which tends to melt under these drying conditions, was cooled quickly in an ice bath and pulverized into 0.17 g (11%) of the brown powder, mp 168 °C. Anal. Calcd for $C_{16}H_{22}F_{12}FeN_4O_2P$: C, 31.14; H, 3.59; Fe, 9.05; N, 9.08. Found: C, 29.15; H, 3.87; Fe, 9.18; N, 9.62. $\Lambda_c = 142$ $\mu\Omega^{-1}$ cm^{-1} at 30 °C and 10^{-3} M in acetone. There is a broad Mössbauer doublet at $\delta = 0.57$ (0.04), $\Delta E_Q = 0.78$ (0.04) mm s^{-1}; $\mu_{\mathrm{eff},298}$(solid) = 4.91 μ_B.

[Fe((acacCl)$_2$trien)](PF$_6$) was prepared by the addition of 0.8 g of *N*-chlorosuccinimide (6 mmol) to a stirred solution of 1.00 g of [Fe((acac)$_2$trien)](PF$_6$) (2 mmol) in 150 ml of CH_2Cl_2. The reaction mixture was refluxed for 1 h, and the solvent was removed without heating. The solid material was treated in the following manner. It was dried in vacuo at 50 °C for 2 h, some impurities were then removed by sublimation at 70 °C over 3 h, it was dried again at 85 °C over another 3 h, and the remaining solid was recrystallized from CH_2Cl_2. The product was again dried in vacuo at 65 °C for 21 h and the remaining impurities were removed by sublimation at 95 °C over 62 h. A second recrystallization from CH_2Cl_2/ethyl ether at 0 °C yielded 0.10 g (9%) of the dark blue crystalline product, mp 230 °C. Anal. Calcd for $C_{16}H_{26}Cl_2F_6FeN_4O_2P$: C, 33.24; H, 4.53; Cl, 12.26; Fe, 9.66; N, 9.69. Found: C, 32.71; H, 4.65; Cl, 12.96; Fe, 9.44; N, 9.66. $\Lambda_c = 149$ $\mu\Omega^{-1}$ cm^{-1} at 30 °C and 10^{-3} M in acetone. There is a broad Mössbauer singlet at $\delta = 0.56$ (0.02) mm s^{-1}; $\mu_{\mathrm{eff},298}$(solid) = 5.98 μ_B.

[Fe((bzacCl)$_2$trien)](PF$_6$) was prepared by the reaction of 0.69 g of *N*-chlorosuccinimide (4.5 mmol) with 1.0 g of [Fe((bzac)$_2$trien)](PF$_6$) (1.6 mmol) in 140 ml of CH_2Cl_2. The stirring solution at room temperature turned green in about 30 s, whereupon the solvent was rapidly removed under vacuum but without heating. The solid material was treated in the following manner. It was dried at 55 °C for 2 h, some impurities were removed by sublimation at 65 °C over 18 h, and then it was dried at 75 °C over 19 h, at 85 °C over 4 h, and finally at 97 °C for 30 h. Recrystallization from CH_2Cl_2/ethyl ether at 0 °C and drying in vacuo over P_2O_5 at 117 °C for 30 h yielded 0.13 g (12%) of the light green product, mp 168 °C dec. Anal. Calcd for $C_{26}H_{30}F_6FeN_4O_2P$: C, 44.47; H, 4.31; Cl, 10.10; Fe, 7.95; N, 7.98. Found: C, 44.14; H, 4.43; Cl, 9.71; Fe, 7.77; N, 7.98. $\Lambda_c = 147$ $\mu\Omega^{-1}$ cm^{-1} at 30 °C and 10^{-3} M in acetone. Due to the overall low yield of ~3% and, therefore, the limited amount of sample, no Mössbauer data are presently available; $\mu_{\mathrm{eff},298}$(solid) = 4.35 μ_B.

[Fe((acac)$_2$trien)](BPh$_4$) was prepared by metathesis from the PF_6^- salt. To a filtered solution of 3.0 g of [Fe((acac)$_2$trien)](PF$_6$) (5.9 mmol) in 20 ml of acetone was added a filtered solution of 2.4 g of $NaBPh_4$ (7 mmol) in 30 ml of acetone. A precipitate immediately formed and after 30 min was collected, washed with acetone, and dried in vacuo over P_2O_5 at 117 °C for 12 h, yielding 2.4 g (60%) of blue plates, mp 210 °C. Anal. Calcd for $C_{40}H_{48}BFeN_4O_2$: C, 70.29; H, 7.08; Fe, 8.17; N, 8.20. Found: C, 70.33; H, 6.98; Fe, 8.11; N, 8.15. $\Lambda_c = 100$ $\mu\Omega^{-1}$ cm^{-1} at 30 °C and 10^{-3} M in acetone and 124 $\mu\Omega^{-1}$ cm^{-1} at 30 °C and 10^{-3} M in acetonitrile. Mössbauer data showed a broad singlet at $\delta = 0.78$ (0.24) mm s^{-1} and a doublet at $\delta = 0.46$ (0.02) mm s^{-1}, $\Delta E_Q = 2.17$ (0.02) mm s^{-1}; $\mu_{\mathrm{eff},298}$(solid) = 3.04 μ_B.

[Fe((acac)$_2$trien)]Br was prepared by metathesis from the PF_6^- salt. To a filtered solution of 1.01 g of [Fe((acac)$_2$trien)](PF$_6$) (2 mmol) in 20 ml of acetone was added a filtered solution of 0.170 g of LiBr (2.2 mmol) in 20 ml of acetone. A precipitate immediately formed and after 10 min at 0 °C was collected and washed with two 15-ml portions of cold acetone and then with large amounts of ethyl ether. Drying in vacuo over P_2O_5 at 117 °C for 8 h yielded 0.59 g (67%) of purple crystals, mp 237 °C. Anal. Calcd for $C_{16}H_{28}BrFeN_4O_2$: C, 43.27; H, 6.35; Br, 17.99; Fe, 12.57; N, 12.61. Found: C, 43.47; H, 6.42; Br, 18.81; Fe, 12.18; N, 12.75. $\Lambda_c = 152$ $\mu\Omega^{-1}$ cm^{-1} at 30 °C and 10^{-3} M in acetonitrile. There is a broad Mössbauer singlet at $\delta = 0.65$ (0.02) mm s^{-1}; $\mu_{\mathrm{eff},298}$(solid) = 5.96 μ_B.

[Fe((acac)$_2$trien)]I was prepared by metathesis from the PF_6^- salt. To a filtered solution of 1.01 g of [Fe(acac)$_2$trien)](PF$_6$) (2 mmol) in 30 ml of acetone was added a filtered solution of 0.33 g of NaI (2.2 mmol) in 15 ml of acetone. After 30 min at 0 °C, the precipitate was collected, washed with small amounts of cold acetone, and then washed with large amounts of ethyl ether. Drying in vacuo over P_2O_5 at 117 °C for 50 h yielded 0.71 g (72%) of slightly hygroscopic purple crystals, mp 265 °C. Anal. Calcd for $C_{16}H_{28}FeIN_4O_2$: C, 39.13; H, 5.75; Fe, 11.37; I, 25.84; N, 11.41. Found: C, 39.35; H, 5.69; Fe, 11.23; I, 26.00; N, 11.37. $\Lambda_c = 167$ $\mu\Omega^{-1}$ cm^{-1} at 30 °C and 10^{-3} M in acetonitrile. There is a broad Mössbauer singlet at $\delta = 0.63$ (0.02) mm s^{-1}; $\mu_{\mathrm{eff},298}$(solid) = 5.93 μ_B.

Variable-Temperature Susceptibility Data (T in K, χ_M'(cor) in 10^{-6} cgsu mol^{-1}, μ_{eff} in μ_B). [Fe((acac)$_2$trien)](PF$_6$) (acetone): 307.6, 12 770, 5.60; 284.6, 13 290, 5.50; 268.5, 13 660, 5.41; 254.1, 13 920, 5.32; 233.2, 13 800, 5.07; 224.6, 13 810, 4.98; 213.4, 13 630, 4.82; 195.3, 13 760, 4.64.

[Fe((acac)$_2$trien)](PF$_6$) (methanol): 301.8, 10 840, 5.11; 294.7, 10 790, 5.04; 290.0, 10 620, 4.96; 276.0, 10 230, 4.75; 258.8, 9400, 4.41; 255.7, 9230, 4.34; 220.6, 7260, 3.58; 213.2, 6240, 3.26.

[Fe((acac)$_2$trien)](PF$_6$) (acetonitrile): 302.2, 13 430, 5.70; 294.7, 13 720, 5.68; 290.0, 13 840, 5.66; 262.3, 14 630, 5.54; 255.7, 14 700, 5.48; 249.6, 14 840, 5.44; 236.3, 15 270, 5.37.

[Fe((acac)$_2$trien)](PF$_6$) (methylene chloride): 306.1, 13 960, 5.84; 276.0, 15 150, 5.78; 258.8, 16 190, 5.79; 227.7, 17 700, 5.68; 222.1, 18 110, 5.67; 220.6, 17 860, 5.61; 208.3, 19 210, 5.66.

[Fe((acac)$_2$trien)](PF$_6$) (tetrahydrofuran): 311.2, 13,130, 5.71; 265.6; 13 190, 5.29; 261.4, 12 860, 5.18; 249.6, 12 490, 4.99; 236.2, 11 900, 4.74; 227.7, 11 170, 4.51; 222.2, 10 750, 4.37.

[Fe((bzac)$_2$trien)](PF$_6$) (acetone): 307.6, 11 240, 5.26; 284.6, 11 030, 5.01; 268.5, 10 690, 4.79; 254.1, 10 320, 4.58; 233.2, 9680, 4.25; 224.6, 9000, 4.02; 213.4, 8630, 3.84; 195.3, 7403, 3.40.

[Fe((bzac)$_2$trien)](PF$_6$) (methanol/10% acetone): 303.6, 6590, 4.00; 291.4, 6560, 3.91; 282.0, 6400, 3.80; 276.2, 6500, 3.79; 260.5, 6500, 3.68; 237.0, 6220, 3.43; 213.0, 5960, 3.20; 178.6, 5490, 2.80.

[Fe((bzac)$_2$trien)](PF$_6$) (methylene chloride): 303.6, 13 340, 5.71; 291.4, 13 890, 5.69; 282.0, 14 250, 5.67; 276.2, 13 980, 5.56; 260.5, 14 450, 5.49; 237.0, 15 680, 5.45; 213.0, 16 610, 5.32; 178.6, 18 640, 5.16.

[Fe((tfac)$_2$trien)](PF$_6$) (acetone): 303.2, 6310, 3.91; 298.2, 6370, 3.90; 266.9, 6110, 3.61; 242.9, 6260, 3.49; 218.0, 6320, 3.32; 206.4, 6590, 3.30; 181.9, 6930, 3.17; 179.4, 7460, 3.27.

[Fe((acacCl)$_2$trien)](PF$_6$) (acetone): 304.9, 8590, 4.58; 279.7, 8300, 4.31; 261.5, 7810, 4.04; 252.2, 7070, 3.78; 228.1, 6170, 3.35; 226.2, 6120, 3.33; 200.8, 5400, 2.94; 185.4, 5190, 2.77.

[Fe((bzacCl)$_2$trien)](PF$_6$) (acetone): 303.2, 7930, 4.38; 298.2, 8000, 4.37; 266.9, 7970, 4.12; 242.9, 8020, 3.95; 218.0, 8570, 3.86; 206.4, 9010, 3.86; 181.9, 9630, 3.74; 179.4, 9664, 3.72.

Results and Discussion

Synthetic and Structural Considerations. The five iron(III)–β-ketoimine complexes [Fe((acac)$_2$trien)]$^+$, [Fe((bzac)$_2$trien)]$^+$, [Fe((tfac)$_2$trien)]$^+$, [Fe((acacCl)$_2$trien)]$^+$, and [Fe((bzacCl)$_2$trien)]$^+$ reported here and shown in Figure 1 are synthetically new. The γ-carbon-substituted [Fe((acacCl)$_2$trien)]$^+$ and [Fe((bzacCl)$_2$trien)]$^+$ species have been prepared from their parent compounds by direct NCS chlorination which, to our knowledge, represents one of the first such reported reactions on β-ketoimine chelate rings;[25] however, analogous reactions on β-diketone,[12–15] monothio-β-diketone,[26] and β-diimine[27] chelate rings are well-known. Syntheses of the tris chelates have been previously reported for [Fe(acacCl)$_3$],[14] [Fe(acacBr)$_3$],[12,14] [Fe(acacI)$_3$],[14] [Fe(acacCH$_3$)$_3$],[28,29] [Fe(acacPh)$_3$],[28,29] and [Fe(acacNO$_2$)$_3$],[30] although we have modified several procedures to maximize yields or to improve purity and have prepared the [Fe(acacI)$_3$] complex, for the first time, by the indirect route of first synthesizing the free acacI ligand.[22]

Syntheses of the parent complexes [Fe(acac)$_3$], [Fe((acac)$_2$trien)](PF$_6$), [Fe((bzac)$_2$trien)](PF$_6$), and [Fe((tfac)$_2$trien)](PF$_6$) are straightforward, yielding products whose six-coordinate structures are well-documented or are chemically very similar to related compounds of known structure. In the solid state, the much studied [Fe(acac)$_3$] complex possesses six different Fe–O bonds, ranging from 1.986 to 2.004 Å in length,[31,32] but in solution, the complex is expected to realize D_3 symmetry. A crystal structure of the [Ni((tfac)$_2$trien)] complex[33] has shown the (tfac)$_2$trien ligand to coordinate in the hexadentate and geometrically specific fashion as proposed in Figure 1. As in the case for the Ni(II) complex, it is likely that the two β-ketoimine chelate rings in [Fe((tfac)$_2$trien)]$^+$ are formed by a Schiff base condensation reaction at the methyl carbonyl group, since it has been our experience that in situ syntheses of related compounds lacking an α-methyl carbonyl on the reacting β-diketone have invariably failed. Furthermore, all the Fe(III) complexes of this work containing linear hexadentate ligands derived from trien are similar in structure to the [Fe((XSal)$_2$trien)]$^+$ complexes first described by Das Sarma and Bailar[34] and more recently characterized in greater detail by ourselves[10] because of their anomalous $^2T \rightleftarrows {}^6A$ spin-equilibrium property in the solid and solution states. Since the Sal$_2$trien ligand N$_4$O$_2$ donor atom set and its arrangement of two cis secondary amine nitrogen atoms, two trans imino nitrogen atoms, and two cis hydroxy oxygen atoms are essentially the same as for these new [Fe((acac)$_2$trien)]$^+$, [Fe((bzac)$_2$trien)]$^+$, and [Fe((tfac)$_2$trien)]$^+$ derivatives, it was hoped that they, too, might exhibit magnetically unusual iron centers for our continuing studies of solution-state spin-equilibrium processes. As described below, this expectation has been largely realized. In addition to their spin-equilibrium potential, the X = H complexes of Figure 1 were also attractive to us in that pioneering work by Collman and others on tris(β-diketonato)metal(III)[12–15,23,28–30,35] and tris(monothio-β-diketonato)cobalt(III) complexes[26] had demonstrated a reactivity of the central γ-carbon atom toward substitution by various halogen or pseudohalogen substituents. A synthetic flexibility of this nature for variable-spin complexes, such as these spin-equilibrium Fe(III) complexes, was appealing because X-substituted derivatives of the parent compounds could likely be obtained in order to systematically modify and study the Fe(III) center electronic structure.

The tris chelates [Fe(acacCl)$_3$] and [Fe(acacBr)$_3$] were formed by halogenating [Fe(acac)$_3$] in boiling CCl$_4$ with the appropriate *N*-halosuccinimide. Introduction of a quantitative amount of 4-*tert*-butylcatechol (see Experimental Section), a radical-trapping agent, had no effect on the course of the chlorination, indicating an electrophilic substitution mechanism involving *ionic* Cl$^+$ rather than the free-radical alternative. Additional chemical evidence for an *ionic* mechanism in these chelate ring halogenation reactions has also been cited by Singh and Sahai,[14] who reported that NCS chlorination of [M(acac)$_3$] occurs more readily in methanol than in chloroform. Attempted bromination of [Fe(acac)$_3$] with buffered Br$_2$ resulted in decomposition of the complex, and attempted direct exchange of the halogen atoms in both [Fe(acacCl)$_3$] and [Fe(acacBr)$_3$] to produce [Fe(acacF)$_3$] using alcoholic solutions of AgF resulted in the recovery of the starting iron complex and other uncharacterized products.

Chlorination of [Fe((acac)$_2$trien)](PF$_6$) in CHCl$_3$ proceeds under much less vigorous conditions than are required for [Fe(acac)$_3$], and the chlorination of [Fe((bzac)$_2$trien)](PF$_6$) in CH$_2$Cl$_2$ at room temperature is most facile of all, being almost instantaneous. This general trend in chelate ring reactivities can be rationalized by viewing the β-ketoimine rings as "enamine"-type structures which would be expected to exhibit greater reactivities than the "benzenoid"-type structure ascribed to the β-diketone rings in [Fe(acac)$_3$].[31,32,36] The work-up and purification procedures for the [Fe((acacCl)$_2$trien)]$^+$ and [Fe((bzacCl)$_2$trien)](PF$_6$) crude reaction products, while being straightforward, are arduous, involving multiple drying, sublimation, and recrystallization steps (see Experimental Section); however, these extensive procedures were found necessary to eliminate all succinimide contaminants from the final products.

The bromination of [Fe((acac)$_2$trien)](PF$_6$) and [Fe((bzac)$_2$trien)](PF$_6$) yields green solids which, to date, have not been isolated in pure form since the products have solubilities very similar to those of the succinimide and *N*-bromosuccinimide impurities and since they decompose under extensive drying and sublimation procedures. [Fe(acacBr)$_3$], on the other hand, is the only tris chelate found to be essentially insoluble in acetone, and this fact enables a clean separation of the product from the very soluble succinimide impurities. [Fe(acacBr)$_3$] in its pure crystalline form possesses a distinct odor resembling that of biacetyl, but after 13 months no decomposition or lachrymatory substances were observed as reported by Collman.[12] Powdered crystalline samples of numerous [Fe(acacBr)$_3$] reaction products melted at 158 °C, lower than the melting point of 170 °C claimed by Singh and Sahai.[14]

The attempted iodination of [Fe(acac)$_3$] using *N*-iodosuccinimide in refluxing CCl$_4$ or the use of ICl in buffered acetic acid or methanol did not produce an isolable [Fe(acacI)$_3$] product. The tris iodinated complex was, however, indirectly obtained by first preparing the iodinated free acacI ligand by the method of Kumler.[22] The complex, [Fe(acacI)$_3$], decomposes over a period of 2–3 weeks, evolving molecular iodine.

The nitration of [M(acac)$_3$] complexes to produce [M(acacNO$_2$)$_3$] in acetic anhydride which contains metal nitrate salts has been suggested to proceed via the in situ preparation of AcO$^-$NO$_2$$^+$ at 0 °C,[23] but no kinetic or spectroscopic evidence of this reaction intermediate is known. Attempted nitration of [Fe(acac)$_3$] with Fe(NO$_3$)$_3$·9H$_2$O was unsuccessful and the use of Cu(NO$_3$)$_2$·3H$_2$O resulted in isolation of a green [Cu(acacNO$_2$)$_2$]·H$_2$O product. Following the synthesis for [Cr(acacNO$_2$)$_3$], as reported by Sen and Thankarajan,[23] Drickamer[30] has previously reported the synthesis of [Fe(acacNO$_2$)$_3$]. However, in our hands, this synthesis did not directly yield the desired product, but instead a modified procedure, as described in the Experimental Section, was used to produce [Fe(acacNO$_2$)$_3$] in a moderate (36%) yield. The shelf life of this complex is judged to be no more than 6 weeks, and recrystallization should be commenced immediately after synthesis due to the tendency of the crude product to decompose upon standing. Similar attempts at nitration of [Fe((acac)$_2$trien)]$^+$ resulted in decomposition of the complex, presumably due to acid hydrolysis of the imino linkage in the acetic anhydride/nitric acid medium.

No substitution reactions were attempted on [Fe((tfac)$_2$trien)](PF$_6$) because of the difficulty of obtaining suitable quantities (overall yield is about 10%) of the complex upon which to attempt the expectedly low-yield halogenation reactions that would result from the necessarily extensive purification procedures.

Characterization of the Complexes. Most of the data characterizing the present β-diketone and β-ketoimine complexes of Fe(III) are set out in the Experimental Section. Analytical results and molecular weights determined from mass spectra and osmometric measurements characterize the tris chelates as nonelectrolytes which are monomeric in chloroform. Solid-state magnetic moments are typical of high-spin ^{6}A Fe(III) complexes, being in the spin-only range of 5.89–6.00 μ_B at 298 K. The Mössbauer spectra exhibit broad singlets at room temperature with very weak absorbance and with half-widths at half-height ranging from 0.68 to 1.23 mm s^{-1}. Similar spectra have been reported for [Fe(acac)$_3$][37–40] with the extensively broadened singlet being attributed primarily to partial spin–spin relaxation of magnetic hyperfine interactions associated with electronic states available to the d^5 ion.[39] The isomer shift δ values for the tris complexes range from 0.55 to 0.82 mm s^{-1} relative to a sodium nitroprusside standard; these values are typical of those usually found for high-spin pseudooctahedral Fe(III) complexes.

The analytical data and conductivity measurements in solution for the new β-ketoimine complexes are consistent with their Figure 1 formulation as monomeric, univalent electrolyte species. The room-temperature solid-state magnetic moments are of special interest for the series, spanning a range of 6.00 μ_B for the [Fe((acac)$_2$trien)](PF$_6$) salt to 3.04 μ_B for the analogous BPh$_4$$^-$ derivative. This behavior is reminiscent of that already observed for the structurally related [Fe((XSal)$_2$trien)](Y) series of complexes[10] where a similarly observed range of moments has been well characterized as arising from ^{2}T(ls, $S = ^1/_2$) $\rightleftarrows$ ^{6}A(hs, $S = ^5/_2$) spin equilibria, with compounds exhibiting intermediate moments between the expected ~2.0 μ_B (ls) and 6.0 μ_B (hs) limits being those in the spin-crossover region around room temperature. Thus, it is likely that similar ^{2}T $\rightleftarrows$ ^{6}A phenomena are also operative in the solid state for these [Fe((acac)$_2$trien)]$^+$, [Fe((bzac)$_2$trien)]$^+$, and [Fe((tfac)$_2$trien)]$^+$ compounds and their γ-chlorinated derivatives, although, in solution, variable-temperature magnetic studies (as discussed below) for [Fe((bzacCl)$_2$trien)]$^+$ and [Fe((tfac)$_2$trien)]$^+$ indicate the possibility of an intermediate, i.e., $S = ^3/_2$, spin ground state for these two species. Complete variable-temperature magnetic, Mössbauer, EPR, and ESCA studies, presently in progress, are expected to provide more definitive information for the solid state concerning these $S = ^1/_2$, $^3/_2$, and $^5/_2$ possibilities. The present study, however, focuses mainly on the solution-state behavior of the [Fe((acac)$_2$trien)]$^+$, [Fe((acacCl)$_2$trien)]$^+$, and [Fe((bzac)$_2$trien)]$^+$ species where a ^{2}T($S = ^1/_2$) $\rightleftarrows$ ^{6}A($S = ^5/_2$) spin equilibrium is most certainly present.

In addition to the magnetic moments, the only other characterizing solid-state data presently available for the β-ketoimineiron(III) complexes are their room-temperature Mössbauer spectra. Data for the computer-analyzed spectra are set out in the Experimental Section for each compound studied. Except for the "lower moment" [Fe((acac)$_2$trien)](BPh$_4$) (3.04 μ_B) and [Fe((tfac)$_2$trien)](PF$_6$) (4.91 μ_B) compounds, the Mössbauer spectra of the other β-ketoimine complexes, with μ_{eff} in the 5.9–6.0-μ_B range, closely resemble those of the high-spin tris chelates, being comprised of very broad singlets with δ = 0.48–0.65 mm s^{-1}. The [Fe((acac)$_2$trien)](BPh$_4$) spectrum possesses a broad signal in nearly the same position (δ = 0.78 mm s^{-1}) which can also be assigned to a ^{6}A spin state. In addition, however, on the extreme wings of this broad singlet there are two well-defined signals which appear to be the components of a large quadrupole-split doublet (δ = 0.46 and ΔE_Q = 2.17 mm s^{-1}). This same general Mössbauer pattern has also been reported for the ^{2}T $\rightleftarrows$ ^{6}A spin-equilibrium [Fe(Sal$_2$trien)](PF$_6$) complex where variable-temperature magnetic and Mössbauer studies have permitted an unambiguous assignment of the quadrupole-split doublet (ΔE_Q = 2.97 mm s^{-1}) to a ^{2}T($S = ^1/_2$) low-spin state.[10] Thus, by analogy, the quadrupole-split doublet in the [Fe((acac)$_2$trien)](BPh$_4$) spectrum is also tentatively assigned to the low-spin ^{2}T state which should be ~83% populated, judging by the 3.04-μ_B magnetic moment at room temperature. The presence of both low-spin and high-spin Mössbauer signals for this BPh$_4$$^-$ compound is significant since it implies that, in the *solid* state for a *dynamic* ^{2}T($S = ^1/_2$) $\rightleftarrows$ ^{6}A($S = ^5/_2$) spin-equilibrium process, the spin-state lifetimes, τ(^{2}T) and τ(^{6}A), are longer than the ~10^{-7} s Mössbauer observation time scale. A similar result has also been found for the [Fe(Sal$_2$trien)](PF$_6$) complex and, indeed, for all other spin-equilibrium iron systems except perhaps the tris(dithiocarbamato)iron(III)[41] and tris(monothiocarbamato)iron(III)[49] complexes. In contrast, *in solution the spin-state lifetimes for the [Fe((acac)$_2$trien)]$^+$ complex are apparently shorter than in the solid state*, being ≤10^{-7} s as measured directly by laser Raman temperature-jump kinetics at 25 °C (see spin-state discussion below). Finally, the Mössbauer spectrum of the [Fe((tfac)$_2$trien)](PF$_6$) complex at room temperature consists of a rather closely spaced asymmetric doublet (δ = 0.57 and ΔE_Q = 0.78 mm s^{-1}) which has little featural resemblance to any of the ^{2}T($S = ^1/_2$) $\rightleftarrows$ ^{6}A($S = ^5/_2$) spectra discussed above; its interpretation is, therefore, deferred to future work.

The solid-state infrared spectra of the γ-substituted tris chelates each exhibit a strong singlet between 1500 and 1600 cm^{-1} characteristic of γ-substituted metal acetylacetonates.[42] In this same region, [Fe(acac)$_3$] exhibits a strong doublet similar to that found for [Co(acac)$_3$] and [Cr(acac)$_3$]. The γ-C–H in-plane bend at 1190 cm^{-1} (compare to that of the mesitylene ring C–H at 1155 cm^{-1}) which is present in the [Fe(acac)$_3$] spectrum is absent from the spectra of the other tris chelates, as expected from their substitution at the γ position. The N–H stretching mode of the trien backbone in the β-ketoimine complexes appears as a singlet in the spectra of [Fe((acac)$_2$trien)](PF$_6$) (3420 cm^{-1}), [Fe((bzac)$_2$trien)](PF$_6$) (3418 cm^{-1}), and [Fe-

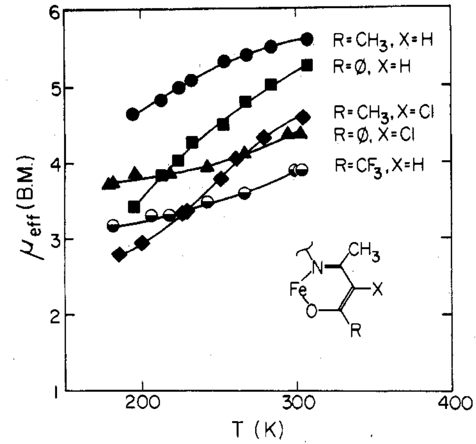


Figure 2. μ_{eff} vs. temperature plots for the magnetically anomalous β-ketoimineiron(III) compounds as their PF_6^- salts in acetone.

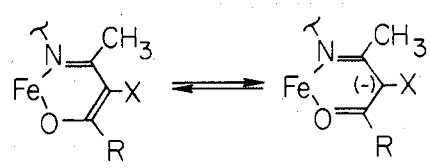
((acacCl)$_2$trien)](PF$_6$) (3310 cm^{-1}) and as a doublet for the complexes [Fe((acac)$_2$trien)](BPh$_4$) (3255, 3265 cm^{-1}), [Fe((acac)$_2$trien)]Br (3092, 3148 cm^{-1}), [Fe((acac)$_2$trien)]I (3112, 3178 cm^{-1}), [Fe((bzacCl)$_2$trien)](PF$_6$) (3292, 3300 cm^{-1}), and [Fe((tfac)$_2$trien)](PF$_6$) (3305, 3408 cm^{-1}). All of the complexes exhibiting any appreciable low-spin character, as evidenced by solid-state magnetic moments below about 5.91 μ_B, display doublets in this region of the infrared, but the "fully" high-spin complexes with $\mu_{eff} \geq 5.91$ μ_B apparently may exhibit either singlets or doublets. Thus, there is no obvious correlation between the degree of multiplicity in the N–H stretching pattern and the Fe(III) spin state as reported for the [Fe(Sal$_2$trien)](Y)·nH$_2$O series of complexes.[10]

Spin State and Electronic Structure Considerations. Complete solution-state variable-temperature magnetic susceptibility data for the five β-ketoimineiron(III) complexes are presented in the Experimental Section. The non-Curie behavior displayed by the compounds, as their PF_6^- salts in acetone, is shown in Figure 2. Magnetic data for the tris(β-diketonato)iron(III) species have not been as extensively documented since these compounds display normal Curie-type behavior for high-spin $S = {}^5/_2$ centers, with moments ranging between 5.6 and 5.9 μ_B from 190 to 300 K. For the [Fe((acac)$_2$trien)]$^+$, [Fe((bzac)$_2$trien)]$^+$, and [Fe((acacCl)$_2$trien)]$^+$ complexes in acetone, the μ_{eff} values span a range of ~2.7–5.6 μ_B, with the observed pattern of decreasing moment with decreasing temperature being characteristic of a spin-equilibrium process, e.g., $^2T(S = {}^1/_2) \rightleftarrows {}^6A(S = {}^5/_2)$. The reversible thermochroism accompanying these processes of red (RT) ⇄ blue (−80 °C) (RT = room temperature) for [Fe((acac)$_2$trien)]$^+$, of red (RT) ⇄ blue (−80 °C) for [Fe((bzac)$_2$trien)]$^+$, and of blue (RT) ⇄ emerald green (−80 °C) for [Fe((acacCl)$_2$trien)]$^+$ is an especially striking property of the systems and parallels that displayed by the $^2T \rightleftarrows {}^6A$ [Fe((XSal)$_2$trien)]$^+$ complexes.[10] The [Fe((bzacCl)$_2$trien)]$^+$ and [Fe((tfac)$_2$trien)]$^+$ complexes of Figure 2 also appear magnetically anomalous, but with a less pronounced temperature dependence, which results in a crossing of their μ_{eff} vs. T curves with those curves of the other three members of the series; in addition, these two complexes do not exhibit a detectable thermochroism in that their acetone solutions remain green and red, respectively, throughout the temperature interval studied.

The μ_{eff} vs. T curves for the [Fe((acac)$_2$trien)]$^+$, [Fe((bzac)$_2$trien)]$^+$, and [Fe((acacCl)$_2$trien)]$^+$ complexes generally parallel one another and are noticeably devoid of the abrupt discontinuities that often characterize spin-equilibrium magnetic data in the solid state.[5] In general, the curves resemble those found for the structurally similar $^2T \rightleftarrows {}^6A$ [Fe((XSal)$_2$trien)]$^+$ compounds, except that the change in moment with temperature is more gradual for the present series. For this reason, the expected $S = {}^1/_2$ low-spin value of ~2.0 μ_B is not actually achieved by any of the three compounds by 190 K, although in the extrapolated low-temperature limit, 2.0 μ_B would seem to be a reasonable limiting value. Thus, with an extrapolated low-temperature limit of 2.0 μ_B and with a high-temperature limit of 5.9–6.0 μ_B (Figure 2), these [Fe((acac)$_2$trien)]$^+$, [Fe((bzac)$_2$trien)]$^+$, and [Fe((acacCl)$_2$trien)]$^+$ complexes are undoubtedly best considered as $^2T(S = {}^1/_2) \rightleftarrows {}^6A(S = {}^5/_2)$ spin-equilibrium species. However, it should be noted that all of these β-ketoimineiron(III) complexes are tetragonally distorted so that the actual $S = {}^1/_2$ electronic ground state is either a ^2E or a ^2A state arising from the octahedral ^2T state. Detailed structural information is not yet available for any of these Fe(III) species,[50] but in the case of the [Ni((tfac)$_2$trien)] complex, the degree of this distortion is reflected by Ni–N(amine), Ni–N(imine), and Ni–O bond distances of 2.13, 2.04, and 2.04 Å, respectively.[33]

For these ^2T (or ^2E, ^2A) $\rightleftarrows$ ^6A complexes, it is of interest to observe the systematic effects of the R and X chelate ring substituents on the Fe(III) spin state. Since the low-spin isomer population for a given temperature increases according to the substituent pattern X = Cl, R = CH$_3$ > X = H, R = Ph > X = H, R = CH$_3$, it appears that electron-withdrawing substituents (assuming Ph > CH$_3$) produce the strongest ligand fields and, thus, the largest low-spin populations. This general pattern parallels that found for the [Fe((XSal)$_2$trien)]$^+$ complexes where the low-spin form is favored according to X = NO$_2$ > H > OCH$_3$. Implicit in this finding is that Fe→ligand (π) bonding is strongly influential in the observed substituent effect with electron-withdrawing groups on the β-ketoimine rings serving to encourage Fe→ligand (π) bonding, thereby providing a reasonable mechanism for an increase in the ligand field strength. On the other hand, electronegative substituents would tend to have an opposite effect on the Fe←ligand (σ) bonding scheme, producing weaker fields through decreased donor atom basicities. For this reason, it is felt that the major substituent effect controlling these spin equilibrium processes is one of Fe→ligand (π) back-bonding in origin.

A γ-carbon substituent, while in the most remote position from the iron atom, is involved in any Fe→ligand (π) scheme by way of the "keto" resonance form (B). While the x-ray



A B

structure[33] of the [Ni((tfac)$_2$trien)] complex (the only useful comparative structure elucidated to date) clearly supports the A "enamine" form as the predominant resonance form, some contribution from B must also be considered likely. In fact, B is an especially compelling form to promote an electrophilic attack on the X = H parent compounds when producing the [Fe((acacCl)$_2$trien)]$^+$ and [Fe((bzacCl)$_2$trien)]$^+$ halogenated derivatives. Furthermore, it can be speculated that the contribution of B may be spin-state dependent and, therefore, that electrophilic substitution processes may have "unusual" temperature dependency for variable-spin compounds such as these β-ketoimine Fe(III) species in comparison to other spin-invariant cases. This interesting possibility is being pursued.

Perhaps the most significant substituent effect occurs for the [Fe((bzacCl)$_2$trien)]$^+$ and [Fe((tfac)$_2$trien)]$^+$ complexes which possess some of the most electron-withdrawing R and

Table I. Thermodynamic Parameters for the Spin-Equilibrium Processes in Solution[a]

Compd	Solvent	$\Delta H°$, kcal mol^{-1}	$\Delta S°$,[b] eu
$[Fe((acac)_2trien)](PF_6)$	Acetone	2.00 (0.08)	10.41 (0.33)
	CH_2Cl_2	1.73 (0.24)	12.44 (0.94)
	CH_3CN	2.36 (0.09)	12.56 (0.34)
	CH_3OH	3.12 (0.07)	12.12 (0.27)
	THF	3.35 (0.13)	14.95 (0.55)
$[Fe((bzac)_2trien)](PF_6)$	Acetone	2.45 (0.08)	10.14 (0.31)
	CH_2Cl_2	1.40 (0.24)	9.24 (0.91)
	CH_3OH/10% acetone	1.28 (0.02)	3.26 (0.09)
$[Fe((acacCl)_2trien)](PF_6)$	Acetone	2.23 (0.09)	7.63 (0.37)
$[Fe((bzacCl)_2trien)](PF_6)$	Acetone[c,d]	0.66 (0.09)	1.99 (0.36)
$[Fe((tfac)_2trien)](PF_6)$	Acetone[c,e]	0.76 (0.10)	1.26 (0.40)

[a] Equilibrium constants were calculated by the equation $K = (\mu_{eff}^2 - \mu_{ls}^2)/(\mu_{hs}^2 - \mu_{eff}^2)$, where μ_{hs} is taken to be 5.91 μ_B and μ_{ls} is taken as 2.00 μ_B with $\Delta S°$ and $\Delta H°$ then obtained from least-squares fits of $-RT \ln K = \Delta G° = \Delta H° - T\Delta S°$. Standard deviations of $\Delta H°$ and $\Delta S°$ from the linear fit are parenthesized. [b] The "electronic entropy" contribution to the $\Delta S°$ of a ^2T(low spin) $\rightleftarrows$ ^6A(high spin) process is $R \ln (6/6)$ or 0. [c] An assumed low-spin value of 2.0 μ_B, as described in footnote *a*, may be unrealistic in this case (see text). [d] Using a low-spin value of 3.72 μ_B as obtained from Figure 2, $\Delta H° = 3.11$ (0.28) kcal mol^{-1} and $\Delta S° = 8.20$ (1.10) eu. [e] Using a low-spin value of 3.17 μ_B as obtained from Figure 2, $\Delta H° = 2.34$ (0.22) kcal mol^{-1} and $\Delta S° = 4.99$ (0.89) eu.

X group combinations of the series. The results of this effect are reflected in Figure 2 where it is obvious that the μ_{eff} vs. *T* curves for these two compounds are still magnetically anomalous but with a less pronounced temperature dependency than for the other three $^2T \rightleftarrows {}^6A$ spin-equilibrium complexes. In addition, the low-temperature limiting magnetic moment for these compounds would appear to be between 3.0 and 4.0 μ_B. Since a value of >3.0 μ_B is too high to be characteristic of an $S = {}^1/_2$ ground state (even considering a large orbital contribution to the 1.73-μ_B spin-only moment[43]), the possibility of a ground state of higher spin multiplicity, such as an $S = {}^3/_2$ state (μ_{eff}(s.o.) = 3.87 μ_B), must be considered. Whatever the case, it is clear that available Mössbauer and solution magnetic susceptibility data point to the $[Fe((bzacCl)_2trien)]^+$ and $[Fe((tfac)_2trien)]^+$ derivatives as being electronically different from the three other $^2T \rightleftarrows {}^6A$ spin-equilibrium compounds of the series. However, more extensive variable-temperature solid-state data will be needed to unravel this difference in detail.

Room-temperature solution moments for the $[Fe((acac)_2trien)](Y)$ complexes ($Y^- = PF_6^-$, BPh_4^-, Br^-, I^-) are found to be somewhat more anion dependent than for the corresponding $[Fe(Sal_2trien)](Y)$ series. For example, in acetonitrile, the range of moments for $[Fe(Sal_2trien)](Y)$ is 4.93 μ_B ($Y^- = Cl^-$) to 5.16 μ_B ($Y^- = BPh_4^-$) whereas, for $[Fe((acac)_2trien)](Y)$, the range is from 5.50 μ_B ($Y^- = Br^-$) to 5.79 μ_B ($Y^- = Cl^-$). In both cases, the ranges are clearly wider than can be explained by the maximum experimental error of about 0.1 μ_B for the Evans method. Since both Fe(III) series exhibit the same anion ordering in acetonitrile, the differences noted may well reflect the effect of varying degrees of $\{[Fe(III)\ complex]^+ \cdot anion\}$ association on the spin equilibria. The wider range of moments observed for the $[Fe((acac)_2trien)]^+$ complex is particularly interesting because of the much closer proximity of the range to the high-spin moment limit of about 6.0 μ_B. By assuming low- and high-spin limits on the magnetic moments of a spin-equilibrium species, an equilibrium constant may be determined from the equation K_{eq} = [high spin]/[low spin] = $(\mu^2 - \mu_{ls}^2)/(\mu_{hs}^2 - \mu^2)$. By use of limits of 2.0 and 5.91 μ_B for the low- and high-spin moment limits, respectively, the room-temperature equilibrium constants for the $[Fe((acac)_2trien)](Y)$ complexes range from 5.5 for $Y^- = Br^-$ to 20 for $Y^- = BPh_4^-$, wider by any measure than the similar range for the $[Fe(Sal_2trien)](Y)$ complexes of 1.9 for $Y^- = Cl^-$ to 2.7 for $Y^- = BPh_4^-$.

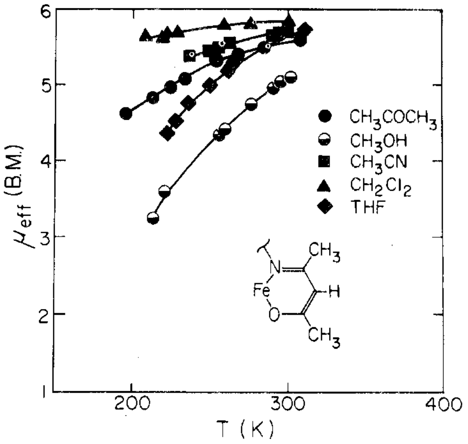


Figure 3. Solvent dependency of the μ_{eff} vs. temperature plots for the $[Fe((acac)_2trien)](PF_6)$ compound.

Thermodynamic parameters characterizing the spin equilibria in various solvents, as derived from their temperature-dependent equilibrium constants, are found in Table I. The calculated $\Delta H°$ and $\Delta S°$ values for the $[Fe((acac)_2trien)]^+$, $[Fe((acacCl)_2trien)]^+$, and $[Fe((bzac)_2trien)]^+$ complexes are similar to those found for the $[Fe((XSal)_2trien)]^+$ series, except that both the $\Delta H°$ and the $\Delta S°$ values for the present series are somewhat smaller, with $\Delta H°$ being only half as large in some cases. Qualitatively, it is likely that the major contribution to $\Delta H°$ arises from the changing Fe–(donor atom) bond distances and energies that are known to accompany the spin-interconversion processes.[44] This being the case, it could be predicted that the overall Fe–N and Fe–O bond distance changes upon spin conversion, for the present $^2T \rightleftarrows {}^6A$ β-ketoimine complexes, might be considerably less than for the $[Fe((XSal)_2trien)]^+$ complexes. Single-crystal x-ray structure studies on compounds of both series are presently under way to test this possibility. The $\Delta S°$ values in Table I are rough indicators of the magnitude of temperature dependency on the magnetic moment. Contained in these values is the "electronic entropy change" of $R \ln (6/6)$ or 0 expected for a $^2T \rightleftarrows {}^6A$ process. In reality, this electronic contribution is probably larger for the present tetragonally distorted complexes since the spin equilibria are actually $^2E \rightleftarrows {}^6A$ [$R \ln (6/4) = 0.80$ eu] or $^2A \rightleftarrows {}^6A$ [$R \ln (6/2) = 2.18$ eu] cases. The remaining, and therefore major, contribution to $\Delta S°$ likely arises from solvation-sphere reorganization processes that accompany spin conversion. Thus, a small solvent and substituent dependency on $\Delta S°$, as observed in most cases, is not unexpected. However, the effect of the CH_3OH/10% acetone solvent mixture on $\Delta S°$ for $[Fe((bzac)_2trien)](PF_6)$ does appear unusually large and surprising. The unusually low $\Delta H°$ and $\Delta S°$ values calculated for the $[Fe((bzacCl)_2trien)]^+$ and $[Fe((tfac)_2trien)]^+$ compounds once again serve to set them apart as being electronically different from the other three $^2T \rightleftarrows {}^6A$ derivatives in the table.

The solvent dependency of the $^2T \rightleftarrows {}^6A$ spin equilibrium for the $[Fe((acac)_2trien)](PF_6)$ complex is shown in Figure 3. The μ_{eff} vs. *T* curves are nonintersecting, except for the THF solution in which the $\Delta H°$ and $\Delta S°$ parameters are the largest of any solvent system investigated. In general, the same solvent effect trend was also noted for the $[Fe(Sal_2trien)](PF_6)$ compound where the high-spin population characteristically decreases according to the solvent series: $CH_2Cl_2 > CH_3CN \sim$ acetone $> CH_3OH$. For both the $[Fe(Sal_2trien)]^+$ and

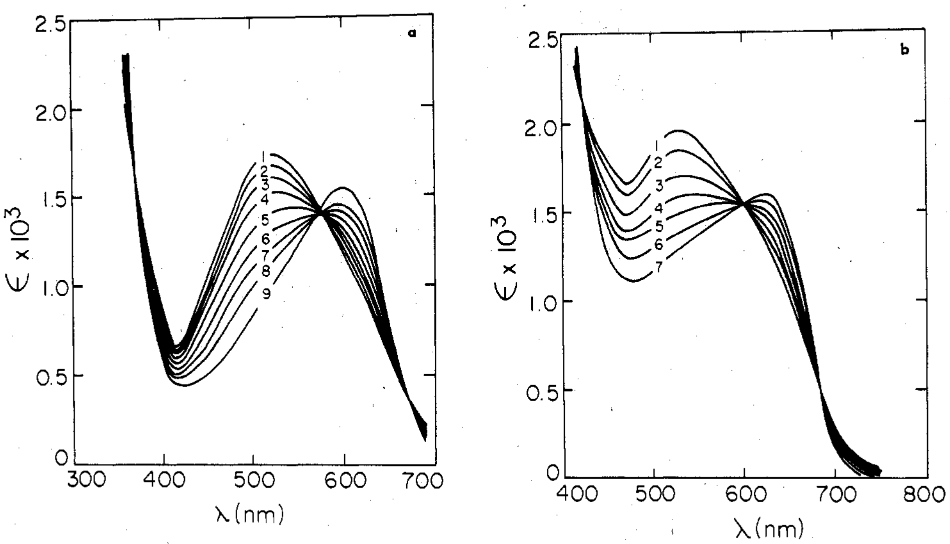


Figure 4. (a) Variable-temperature electronic spectrum of $[Fe((acac)_2trien)](PF_6)$ in methanol at (1) 294 K, (2) 282 K, (3) 272 K, (4) 262 K, (5) 251 K, (6) 240 K, (7) 231 K, (8) 223 K, and (9) 206 K. (b) Variable-temperature electronic spectrum of $[Fe((bzac)_2trien)](PF_6)$ in methanol at (1) 295 K, (2) 279 K, (3) 263 K, (4) 250 K, (5) 242 K, (6) 231 K, and (7) 221 K.

$[Fe((acac)_2trien)]^+$ cations, examination of molecular models reveals that a particularly inviting site for a specific $\{[Fe(III)\ complex]^+\cdot solvent\}$ interaction might be at the coordinated secondary amine protons of the trien backbone. In fact, for $[Fe(Sal_2trien)]^+$ a linear correlation was found between the N–H stretching frequency in the infrared spectrum and the compounds's magnetic moment in various solvents, suggesting that [N–H···solvent] hydrogen-bonding interactions of ≤ 5 kcal mol^{-1} are highly influential in determining the final low- and high-spin isomer distributions.[10] For $[Fe((acac)_2trien)](PF_6)$ in six solvent systems, the corresponding $\mu_{eff,295}$ and ν_{N-H}(str) values are as follows: CH_2Cl_2, 5.83 μ_B, 3303 cm^{-1}; $PhNO_2$, 5.72 μ_B, 3286 cm^{-1}; CH_3CN, 5.71 μ_B, 3270 cm^{-1}; THF, 5.60 μ_B, 3297 cm^{-1}; acetone, 5.58 μ_B, 3285 cm^{-1}; 50:50 acetone-d_6/D_2O by mole percent, 5.44 μ_B, 3261 cm^{-1}. It is clear from these data that no exact linear correlation exists between the two parameters, although, qualitatively, the stronger hydrogen-bonding solvents (largest $\Delta\nu_{N-H}$(str) values) do produce the larger low-spin isomer populations. The solvent choice is, thus, an important and generally useful working parameter for adjusting the equilibrium position of these Fe(III) ls $\rightleftarrows$ hs processes.

The temperature-dependent electronic spectra in the 300–700-nm range for the two $^2T \rightleftarrows {}^6A$ compounds, $[Fe((acac)_2trien)](PF_6)$ and $[Fe((bzac)_2trien)](PF_6)$, in methanol, are shown in Figure 4. The general nature of the spectral changes with temperature is immediately apparent, and it is the magnitude of these changes that gives rise to the striking thermochromism that is associated with the spin equilibria. Because the higher energy bands at 520–540 nm are found to decrease steadily in intensity with decreasing temperature and moment, they are assigned to the high-spin form. Conversely, the lower energy bands at 610–640 nm increase steadily in intensity with decreasing temperature and moment, permitting assignment mainly to the low-spin form. With extinction coefficients of 500–2000, these low- and high-spin bands are undoubtedly metal–ligand charge transfer in origin, and a careful search on the low-energy side of the low-spin band revealed no lower intensity bands of purely "d–d" character. Data in Table II showing the solvent dependency on the electronic spectrum and magnetic moment for the $[Fe((acac)_2trien)](PF_6)$ complex serves to emphasize again the interrelationship between the Fe(III) spin state, the solvent system, and the variable-temperature electronic spectrum of these spin-equilibrium processes.

Table II. Solvent Dependency on the Magnetic Moment and Electronic Spectrum of the $[Fe((acac)_2trien)](PF_6)$ Complex

Solvent	$\mu_{eff,295}$, μ_B	High-spin mole fraction (295 K)^a	ϵ(λ 522 nm) (295 K)^b
CH_2Cl_2	5.83	0.96	2610
CH_3CN	5.71	0.91	2430
THF	5.60	0.89	2370
Acetone	5.58	0.86	2390
DMSO	5.41	0.79	2150
CH_3OH	5.02	0.68	1800

^{a} Calculated from magnetic moment data assuming $\mu_{eff}(ls) = 2.00\ \mu_B$ and $\mu_{eff}(hs) = 5.91\ \mu_B$. ^{b} Absorbance at 522 nm from Figure 4a is assigned to the high-spin form.

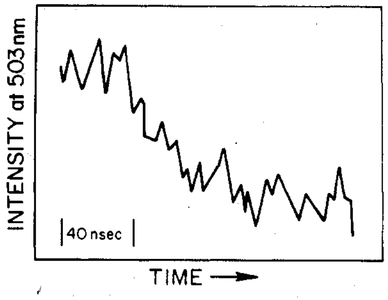


Figure 5. A typical temperature-jump relaxation trace obtained at 503 nm for the $[Fe((acac)_2trien)](PF_6)$ compound in methanol/10% acetone.

As part of our continuing study into the electronic and structural factors which determine dynamic spin-state lifetimes for variable-spin metal complexes, direct measurement of the lifetimes, $\tau(^2T)$ and $\tau(^6A)$, for the $[Fe((acac)_2trien)]^+$ complex in methanol/10% acetone have been obtained by the laser Raman temperature-jump method. The experimental details and conditions used for the measurements are set out in the Experimental Section; the relaxation traces were obtained by monitoring the temperature-dependent spectral changes at 503 nm with time (ns). A typical experimental trace is shown in Figure 5. Using this technique, $\tau(^2T)$ and $\tau(^6A)$ have been determined to be 6.7×10^{-8} and 1.5×10^{-7} s, respectively, for the $[Fe((acac)_2trien)](PF_6)$ salt in methanol/10% acetone at 25 °C. These spin-state lifetimes are very similar to those already obtained for the $[Fe(Sal_2trien)](PF_6)$ compound in methanol at 20 °C with $\tau(^2T) = 7.1 \times 10^{-8}$ s and $\tau(^6A) = 6.7 \times 10^{-8}$ s.[10] The presence of similar spin lifetimes for the two complexes is not too surprising since both of the Fe(III)

${}^2\mathrm{T} \rightleftarrows {}^6\mathrm{A}$ ($\Delta S = 2$, two-electron spin change) spin equilibria arise from N_4O_2 donor atom sets belonging to structurally similar, chelated, linear hexadentate ligands. However, it is interesting to note that attempts to obtain lifetimes for the [Fe((bzac)$_2$trien)](PF$_6$) complex under similar conditions were unsuccessful, possibly due to a spin-relaxation time that is faster than the heating rise time of the experiment (~25–30 ns)[21,51] or perhaps just to an unfavorable K_{eq}

$${}^2\mathrm{T} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} {}^6\mathrm{A}$$

for the solvent and temperature combination studied.[45] In preliminary studies we also obtained no measurable relaxation for the tris(*N*,*N*-dimethyldithiocarbamato)iron(III) complex, although in this case the small $\Delta H°$ (1–2 kcal mol^{-1}) and correspondingly small spectral changes with temperature for the ${}^2\mathrm{T} \rightleftarrows {}^6\mathrm{A}$ process could also contribute to the lack of an observable relaxation trace.[46] The only other $\Delta S = 2$ spin change events for which comparable lifetime data are presently available are for two Fe(II) ${}^1\mathrm{A} \rightleftarrows {}^5\mathrm{T}$ (or ${}^5\mathrm{A}$) systems: [Fe(6-Mepy)$_2$(py)tren]$^{2+}$ ($\tau({}^1\mathrm{A}) = 2.5 \times 10^{-7}$ s and $\tau({}^5\mathrm{A}) = 2.0 \times 10^{-7}$ s)[9] and the bis[hydrotris(pyrazolyl)borate]iron(II) complex ($\tau({}^1\mathrm{A}) = 1.0 \times 10^{-7}$ s and $\tau({}^5\mathrm{A}) = 5.0 \times 10^{-8}$ s).[47] Thus, these data suggest that solution spin-state lifetimes for simple inorganic Fe(II) and Fe(III) $\Delta S = 2$ spin equilibria span a considerable range, with the lower limit possibly being unattainable by the laser Raman *T*-jump method and with a probable upper limit of ~10^{-6} s. Work is continuing on the development of new synthetic iron (ΔS = 1 and 2) and cobalt ($\Delta S = 1$) systems, of varying electronic structure and geometry, for further comparative studies. In this regard, variable-spin metalloproteins will also be of special interest.[48]

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Registry No. [Fe(acacCl)$_3$], 15169-14-9; [Fe(acacBr)$_3$], 15169-15-0; [Fe(acacI)$_3$], 15169-16-1; [Fe(acacCH$_3$)$_3$], 13978-46-6; [Fe(acacPh)$_3$], 15713-87-8; [Fe(acacNO$_2$)$_3$], 15169-26-3; [Fe((acac)$_2$trien)](PF$_6$), 60209-56-5; [Fe((bzac)$_2$trien)](PF$_6$), 60224-25-1; [Fe((tfac)$_2$trien)](PF$_6$), 60224-23-9; [Fe((acacCl)$_2$trien)](PF$_6$), 60209-51-0; [Fe((bzacCl)$_2$trien)](PF$_6$), 60209-49-6; [Fe((acac)$_2$trien)](BPh$_4$), 60209-55-4; [Fe((acac)$_2$trien)]Br, 60209-52-1; [Fe((acac)$_2$trien)]I, 60209-53-2; [Fe(acac)$_3$], 14024-18-1; *N*-chlorosuccinimide, 128-09-6; *N*-bromosuccinimide, 128-08-5.

References and Notes

(1) Presented in part at the Centennial National Meeting of the American Chemical Society, New York, N.Y., April 1976; see Abstracts, No. INOR 47.
(2) Robert A. Welch Foundation Graduate Fellow, 1975–present.
(3) Robert A. Welch Foundation Undergraduate Fellow, Summer 1975.
(4) L. Cambi and L. Szego, *Ber. Dtsch. Chem. Ges.*, **64**, 2591 (1931).
(5) R. L. Martin and A. H. White, *Transition Met. Chem.*, 4 (1968).
(6) E. K. Barefield, D. H. Busch, and S. M. Nelson, *Q. Rev., Chem. Soc.*, **22**, 457 (1968).
(7) M. A. Hoselton, L. J. Wilson, and R. S. Drago, *J. Am. Chem. Soc.*, **97**, 1722 (1975).
(8) L. J. Wilson, D. Georges, and M. A. Hoselton, *Inorg. Chem.*, **14**, 2968 (1975).
(9) M. A. Hoselton, R. S. Drago, L. J. Wilson, and N. Sutin, *J. Am. Chem. Soc.*, in press.
(10) M. F. Tweedle and L. J. Wilson, *J. Am. Chem. Soc.*, **98**, 4824 (1976).
(11) S. C. Cummings and R. E. Sievers, *Inorg. Chem.*, **11**, 1483 (1972).
(12) J. P. Collman, R. A. Moss, H. Maltz, and C. C. Heindel, *J. Am. Chem. Soc.*, **83**, 531 (1961).
(13) J. P. Collman, *Angew. Chem.*, **77**, 154 (1965).
(14) P. R. Singh and R. Sahai, *Aust. J. Chem.*, **20**, 639 (1967).
(15) P. R. Singh and R. Sahai, *Aust. J. Chem.*, **20**, 649 (1967).
(16) See for example V. V. Komratova, V. A. Grigoreva, A. I. Ivanov, S. M. Baturin, and G. S. Entelis, *Kinet. Katal.*, **11**, 1406 (1970).
(17) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).
(18) D. Ostfeld and I. A. Cohen, *J. Chem. Educ.*, **49**, 829 (1972).
(19) K. Welgehausen, M. L. Rudee, and R. B. McLellan, *Acta Metall.*, **21**, 589 (1973).
(20) B. L. Chrisman and T. A. Tumolillo, *Comput. Phys. Commun.*, **2**, 322 (1975).
(21) D. H. Turner, G. W. Flynn, N. Sutin, and J. V. Beitz, *J. Am. Chem. Soc.*, **94**, 1554 (1972).
(22) W. D. Kumler, *J. Am. Chem. Soc.*, **60**, 855 (1938).
(23) D. N. Sen and N. Thankarajan, *Indian J. Chem.*, **3**, 215 (1965).
(24) J. P. Freeman and I. G. Shepard, "Organic Syntheses", Collect. Vol. V, Wiley, New York, N.Y., p 839.
(25) D. F. Martin, *Prep. Inorg. React.*, **1**, 59 (1964).
(26) A. Yokoyama, S. Kawanishi, M. Chikuma, and H. Tanaka, *Chem. Pharm. Bull.*, **15**, 540 (1967); A. Yokoyama, S. Kawanishi, and H. Tanaka, *ibid.*, **18**, 356 (1970).
(27) W. H. Elfring, Jr., and N. J. Rose, *Inorg. Chem.*, **14**, 2759 (1975).
(28) W. C. Fernelius and B. E. Bryant, *Inorg. Synth.*, **5**, 105 (1967).
(29) J. P. Fackler, *Prog. Inorg. Chem.*, **7**, 361 (1966).
(30) C. W. Frank and H. G. Drickamer, *J. Chem. Phys.*, **56**, 3551 (1972).
(31) R. B. Roof, *Acta Crystallogr.*, **9**, 781 (1956).
(32) J. Iball and C. H. Morgan, *Acta Crystallogr.*, **23**, 239 (1967).
(33) M. F. Richardson, *Can. J. Chem.*, **52**, 3720 (1974).
(34) B. Das Sarma and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **77**, 5476 (1955).
(35) P. C. Doolen and P. H. Gore, *J. Chem. Soc. C*, 211 (1967).
(36) M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, **67**, 2003 (1945).
(37) L. M. Epstein, *J. Chem. Phys.*, **36**, 2731 (1962).
(38) G. K. Wertheim, W. R. Kingston, and R. H. Herber, *J. Chem. Phys.*, **37**, 687 (1962).
(39) J. W. G. Wignall, *J. Chem. Phys.*, **44**, 2462 (1966).
(40) G. M. Bancroft, A. G. Maddock, W. K. Ong, and R. H. Prince, *J. Chem. Soc. A*, 1966 (1967).
(41) R. Richards, C. E. Johnson, and H. A. O. Hill, *J. Chem. Phys.*, **48**, 5231 (1968).
(42) J. P. Collman, *Adv. Chem. Ser.*, **No. 37**, 78 (1963).
(43) B. N. Figgis, *Trans. Faraday Soc.*, **57**, 204 (1961).
(44) For two Fe(II) ${}^1\mathrm{A} \rightleftarrows {}^5\mathrm{T}({}^5\mathrm{A})$ spin-equilibrium processes, variable-temperature structural data for [Fe(bpy)$_2$(NCS)$_2$] [E. Konig and K. J. Watson, *Chem. Phys. Lett.*, **6**, 457 (1970)] and [Fe(6-Mepy)$_3$tren](PF$_6$)$_2$[7] reveal that the average Fe–N bond distances decrease by ≥0.12 Å upon the ${}^5\mathrm{T} \rightarrow {}^1\mathrm{A}$ spin conversion. In comparison, for the tris(*N*,*N*-R$_2$-dithiocarbamato)iron(III) complex (R = ethyl) the average Fe–S bond distances decrease by only ~0.05 Å upon a partial ${}^6\mathrm{A} \rightarrow {}^2\mathrm{T}$ spin conversion [J. G. Leipoldt and P. Coppens, *Inorg. Chem.*, **12**, 2269 (1973)].
(45) For example, assuming an upper limit on the measured relaxation time of $\tau = 30$ ns in methanol/10% acetone solution, upper limits on the spin-state lifetimes, $\tau({}^2\mathrm{T})$ and $\tau({}^6\mathrm{A})$, are calculated as 4.7×10^{-8} and 8.7×10^{-8} s, respectively, using $K_{\mathrm{eq}} = [\mathrm{hs}]/[\mathrm{ls}] = k_1({}^6\mathrm{A})/k_{-1}({}^2\mathrm{T}) = [\tau({}^6\mathrm{A})]^{-1}/[\tau({}^2\mathrm{T})]^{-1} = 0.57$ as calculated from the magnetic susceptibility at 20 °C.
(46) Unpublished results.
(47) J. K. Beattie, N. Sutin, D. H. Turner, and G. W. Flynn, *J. Am. Chem. Soc.*, **95**, 2052 (1973).
(48) J. K. Beattie and R. J. West, *J. Am. Chem. Soc.*, **96**, 1933 (1974), and ref 9.
(49) R. Kunze, D. L. Perry, and L. J. Wilson, submitted for publication in *Inorg. Chem.*
(50) **Note Added in Proof.** Preliminary structural data for the high-spin [Fe((acacCl)$_2$trien)](PF$_6$) compound have confirmed the general structure shown in Figure 1 with the Fe–N(amine), Fe–N(imine), and Fe–O bond distances being ~2.2, 2.1, and 1.9 Å, respectively (private communication, Professor E. Sinn, University of Virginia).
(51) **Note Added in Proof.** Recently, during attempts to reproduce laser T-jump data for the [Fe((acac)$_2$trien)]$^+$ and [Fe((Sal)$_2$trien)]$^+$ complexes, we have observed relaxation traces that indicate $\tau \leq 30$ ns for these spin-relaxation processes also. The reason for the apparent disagreement between these most recent and earlier results is still not certain. It is clear, however, that τ's (relaxation times) of 30–50 ns are at the lower limit of measurability for a T-jump technique, and other kinetic methods such as ultrasonic relaxation ($\tau \gtrsim 5$ ns being measurable) may be required to unambiguously establish spin-state lifetimes for some of these spin-equilibrium processes; such measurements are presently being attempted (private communication, Professor J. K. Beattie, University of Sydney, Sydney, Australia).