compound is obtained by pumping to dryness. It must be protected from light. Freshly prepared, it is colorless like the other salts, but it slowly turns brown, especially in the light.

IR data for $Cs^+C(SO_2CF_3)_3^-$ (in KBr): 2923 w, 2853 w, 1385 s, 1373 vs, 1334 m, 1230 s, 1196 vs, 1131 s, 1121 s, 970 s, 776 w, 765 w, 693 s, 609 s, 584 s, 515 s, 427 w, 393 w, 279 w cm^{-1}. Raman data for $K^+C(SO_2CF_3)_3^-\cdot H_2O$ (solid): 1395 m, 1378 m, 1348 w, 1243 m, 1227 m, 1196 w, 1119, w, sh, 1112 m, 1002 w, 983 w, 773 s, 763 w, sh, 688 m, 577 m, 570 m, sh, 558 m, 535 m, 418 w, 396 m, 384 m, 374 m, 349 s, 329 w, 313 s, 291 s, 275 m, 260 vs, 209 w, 195 m, 187 m, 124 s cm^{-1}.

Anal. Calcd for $C_4F_9O_3S_3Rb$: C, 9.67; F, 34.44; S, 19.34; Rb, 17.22. Found: C, 8.93; F, 34.10; S, 17.78; Rb, 18.47.

Crystallographic Study. A needle-shaped, colorless crystal of $K^+C(SO_2CF_3)_3^-\cdot H_2O$ of approximately 0.3 mm size was obtained by very slow but complete evaporation of the water from an aqueous solution over a period of several days. Intensities were measured on a STOE diffractometer with graphite monochromator, Mo Kα radiation, and Ω scan at room temperature. The space group was determined as $Pc2_1b$ with a = 605.91 (6) pm, b = 1398.77 (8) pm, and c = 1605.60 (13) pm, with a cell volume of 1.36097×10^9 pm^3, $Z = 4$, and calculated density of 2.289 g cm^{-3}. A total of 1255 reflections were measured, 1232 reflections with $I > 2\sigma(I)$; when $+h,+k,+l$, $5° < 2\theta < 50°$. All atoms were anisotropically refined, no extinction corrections were made, and a numerical absorption correction μ = 9.6 cm^{-1} was used. Weighting scheme $W = xy$, $x = 1$ for $\sin\delta > 0.4$, $x = (\sin\delta)/0.4$ for $\sin\delta \leq 0.4$, $y = 1$ for $F_o < 40$, $y = 40/F_o$ for $F_o \geq 40$.

The structure was determined by using a procedure based on intermolecular Patterson vectors, called IMPASS.[8] The method was chosen because the direct methods MULTAN and SHELX failed. Scattering factors from ref 9 were used. The function $\sum w(|F_o| - |F_c|)^2$ was minimized, giving the agreement factors $R = 0.029$, $R_w = 0.028$.

$CCl(SO_2CF_3)_3$. A glass ampule with valve is charged with 0.49 g (0.9 mmol) of $Ag^+C(SO_2CF_3)_3^-$, onto which is condensed 2 mL of dry CH_2Cl_2 and 0.1 g (1.4 mmol) of Cl_2. The suspension is stirred for 2 h at 0 °C. After filtration and evaporation of the solvent from the filtrate, the resulting residue is sublimed from room temperature onto a −30 °C cold finger at 10^{-2} mbar. Colorless $ClC(SO_2CF_3)_3$ is obtained: 0.38 g (90% yield); mp 69.1 °C.

IR data: 2923 w, 2853 w, 2423 w, 1964 w, 1377 vs, 1322 m, 1204 vs, 1124 vs, 983 s, 765 w, 689 m, 630 s, 586 m, 416 w, 386 w cm^{-1}. Raman data: 1418 w, 1407 w, 1220 m, 1194 m, 1095 m, 873 w, 788 w, 770 s, 737 w, 650 w, 582 w, 561 w, 547 w, 525 w, 498 w, 387 s, 367 w, 337 s, 320 m, 301 m, 274 s, 233 s, 200 s, 177 s, 157 vs, 121 w cm^{-1}. ^{19}F NMR data ($CDCl_3$): $\Phi = -60.7$. Mass spectral data: m/e, 297 ($C_3F_6O_3S_2Cl^+$, 2%), 249 ($C_3F_6S_2Cl$, 3%), 145 ($C_2F_3O_2S^+$, 4%), 133 ($CF_3O_2S^+$, 2%), 117 (CF_3OS^+, 10%), 69 (CF_3, 100%).

$CBr(SO_2CF_3)_3$. Bromine (0.2 g, 1.25 mmol) is dissolved in 8 mL of dry CH_2Cl_2 and is slowly added to a suspension of 0.6 g (1.16 mmol) of $Ag^+(SO_2CF_3)_3^-$ in 8 mL of CH_2Cl_2 at 0 °C. Stirring is maintained for 3 h. The precipitate is filtered off and washed with CH_2Cl_2. The combined filtrates are pumped to dryness. The residue is sublimed from room temperature onto a −30 °C cold finger at 10^{-2} mbar. A total yield of 0.44 g (94% yield) of colorless $BrC(SO_2CF_3)_3$ is obtained; mp 93.8 °C.

IR data: 2923 w, 2853 w, 2414 vw, 1972 w, 1378 vs, 1332 m, 1204 vs, 1126 vs, 982 s, 765 w, 689 m, 630 s, 586 s, 516 m, 416 w, 386 w cm^{-1}. Raman data: 1403 m, 1217 m, 1193 w, 1095 m, 808 w, 785 w, 770 m, 730 w, 649 vw, 582 vw, 560 vw, 548 w, 522 vw, 369 s, 320 sh, 311 s, 277 s, 234 vs, 202 vs, 157 vs, 123 cm^{-1}. ^{19}F NMR ($CDCl_3$): $\Phi = -60.3$. Mass spectral data: m/e, 341 ($C_3F_6O_3S_2Br^+$, 2%), 292 ($C_3F_3S_2Br^+$, 1%), 196 (CF_3OSBr^+, 1%), 145 ($C_2F_3O_2S^+$, 12%), 133 ($CF_3O_2S^+$, 6%), 123 ($CSBr^+$, 9%), 107 ($COBr^+$, 16%), 91 (CBr^+, 7%), 69 (CF_3^+, 100%).

Acknowledgment. This research was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Prof. P. Sartori (Universität Duisburg) for samples of CF_3SO_2F and Prof. J. Fuchs (FU Berlin) for help with the crystal structure determination.

Registry No. $HC(SO_2CF_3)_3$, 60805-12-1; $CH_2(SO_2CF_3)_2$, 428-76-2; CF_3SO_2F, 335-05-7; $Cs^+C(SO_2CF_3)_3^-$, 114395-68-5; $K^+C(SO_2CF_3)_3^-$, 114395-69-6; $Rb^+C(SO_2CF_3)_3^-$, 114395-70-9; $Ag^+C(SO_2CF_3)_3^-$, 114395-71-0; $CCl(SO_2CF_3)_3$, 114395-72-1; $CBr(SO_2CF_3)_3$, 114395-73-2.

Supplementary Material Available: Listings of anisotropic thermal parameters, bond lengths, and bond angles and a packing diagram (6 pages); a table of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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A New Class of (*N*,*N*′-Bis(salicylideneamino)ethanato)iron(II) Complexes: Five-Coordinate $[Fe^{II}(salen)L]^-$. Preparation, Properties, and Mechanism of Electron-Transfer Reactions

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Received December 29, 1987

The heterogeneous reaction of the Fe(II) complex Fe(salen) with ligands L^- = F^-, Cl^-, OH^-, NCS^-, CN^-, SH^-, and SR^- in acetonitrile afforded the purplish complexes $[Fe(salen)L]^-$, isolated as sodium or Et_4N^+ salts. Also generated in situ was $[Fe(salen)(OC_6H_4\text{-}p\text{-}Me)]^-$. The complexes contain high-spin Fe(II) in a square-pyramidal coordination unit with an axial L^- ligand, exhibit isotropically shifted ^1H NMR spectra of good resolution, and are electrochemically oxidizable to Fe(salen)L in chemically reversible processes. Absorption and NMR spectra clearly indicate the similarity in structure of the complexes, and the isotropic shifts show that the $S = 2$ ground state, established for one complex in the solid and solution states, applies to all. $(Et_4N)[Fe(5\text{-}NO_2salen)(SC_6H_4\text{-}p\text{-}Me)]$ crystallizes in triclinic space group $P\bar{1}$ with a = 9.644 (2) Å, b = 12.115 (3) Å, c = 14.788 (3) Å, α = 98.33 (2)°, β = 105.84 (2)°, γ = 98.41 (2)°, and $Z = 2$. With use of 3483 unique data ($F_o^2 > 3\sigma(F_o^2)$), the structure was refined to R (R_w) = 4.5% (6.1%). The anion contains Fe(II) in a somewhat distorted-square-pyramidal geometry with the sulfur atom in the axial position. The Fe atom is displaced 0.49 Å above the O_2N_2 mean plane, with a Fe–S bond distance of 2.386 (2) Å. The structure is similar to those of $[Fe(P)SR]^-$ complexes (P = porphyrinate) and is assumed to apply to all members of the set. Selected reactions Fe(salen)L + $[Fe(salen)L']^-$ in acetone result in electron transfer or ligand exchange and have been examined by ^1H NMR spectroscopy. A mechanism involving a doubly bridged binuclear intermediate is proposed and provides fresh insight into how coordinatively unsaturated complexes of this type may undergo electron transfer and ligand exchange.

Introduction

The chemistry of Fe^{III}(salen)L complexes (salen = *N*,*N*′-bis(salicylideneamino)ethanato(2−)) has been extensively investigated since the original synthesis of several examples of this class by Pfeiffer et al., whose major contribution in 1933 in effect opened the field of Schiff base complexes.[2] A large variety of anionic ligands L, including halide, pseudohalide, carboxylate, phenolate, and thiolate, have been shown to form stable, mononuclear, high-spin complexes[2-13] that have a distorted-square-pyramidal

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stereochemistry.[14-16] A second class of mononuclear Fe^{III}(salen) complexes is composed of six-coordinate species.[9-11,17] Both classes have enjoyed extensive utility, especially in the examination of geometrical and electronic structural aspects of Fe(III) in weak ligand fields. Most recently, complexes of these types have figured prominently in the development of models for nonheme dioxygenases by Que and co-workers.[9-12,15,17]

In the course of investigating the formation of the Fe^{III}–S–Fe^{III} bridge as it occurs in $[Fe(salen)]_2S$ and related Schiff base complexes,[18,19] we have made an observation that has led to the discovery of a previously unknown class of Fe(salen) complexes. Reaction of Fe(salen)(OAc) or $[Fe(salen)]_2S$ with 2 equiv of hydrosulfide in DMF solution resulted in the immediate development of an intense purple species subject to one-electron oxidation at a potential more negative than that of the redox couple of the initial complex. Isolation and identification of this species, together with additional experiments, has led to recognition of the complexes $[Fe^{II}(salen)L]^-$, containing anionic ligands L. Several examples of type Fe^{II}(salen)L with a neutral ligand L, introduced separately[6a,20,21] or as part of the fragment bridging the two salicylideneamino groups,[22-24] have been described. Those of the latter sort have distorted-trigonal-bipyramidal structures.[23,24] The corresponding Fe(III) complexes have not been obtained. We report here the synthesis and spectroscopic, magnetic, and redox properties of members of the $[Fe(salen)L]^-$ class of complexes, together with a representative structure of one member. Because these complexes can be reversibly oxidized, it has also been possible to examine the course of electron-transfer reactions with related complexes of the Fe^{III}(salen)L type.

Experimental Section

Preparation of Compounds. The Schiff bases H_2(X-salen) (X = 4-Me, 5-Me, 3-*t*-Bu, 5-*t*-Bu) were prepared as described for related compounds[19] with use of substituted salicylaldehydes obtained by the Duff reaction.[25] $H_2(5\text{-}NO_2salen)$ was prepared similarly from the commercial salicylaldehyde. The compounds 2,6-dimethylbenzenethiol,[26] 2,4,6-triisopropylbenzenethiol,[27] and $NaSSiMe_3$[28] were prepared by published methods. Iron complexes were prepared under anaerobic conditions. Fe(X-salen) (X = 4-Me, 5-Me, 3-*t*-Bu, 5-*t*-Bu, 5-NO_2) were synthesized by equimolar reaction of $Fe(OAc)_2$ and the ligand in hot acetonitrile for 2 h. Products were isolated as flocculent, highly dioxygen-sensitive solids of sufficient purity to be used in the reactions that follow. Fe(salen) has been previously prepared by another procedure.[29] The complexes Fe(salen)L (L = Cl^-,[2a] NCS^-[7]) were obtained by literature methods; Fe(X-salen)Cl (X = 3-*t*-Bu, 5-*t*-Bu, 5-NO_2) were prepared in an analogous manner. Fe(X-salen)(S-*p*-tol) (X = 3-*t*-Bu, 5-*t*-Bu; tol = tolyl) were prepared by the reaction of $Fe_3O(OAc)_7$ with the Schiff base, followed by reaction of *p*-toluenethiol as described for Fe(salen)(SPh).[30] The compounds were obtained as brown crystalline solids after recrystallization from hexane/acetone (2:1 v/v). Substituted Fe(III) salen complexes were utilized to improve solubility in organic solvents (X = 3-*t*-Bu, 5-*t*-Bu) or shift redox potentials in a desired direction (X = 5-NO_2).

$(Et_4N)(SR)$ (R = Ph, *p*-tol). A frequent preparation of these compounds, metathesis of the sodium arenethiolate with a quaternary ammonium salt in acetone, leads to a product contaminated with sodium. When used in the preparations of the Fe(II) complexes that follow, minority fractions of the products were sodium salts. Pure compounds were obtained by use of the thiolate salts prepared as follows. A solution of 4.36 g (0.035 mol) of *p*-toluenethiol in 50 mL of methanol was treated with 10.5 g (0.018 mol) of a 25% solution of Et_4NOH in methanol. The mixture was stirred for 1 h, the solvent was removed in vacuo at 40 °C, and the resultant yellow syrup was washed with ether. The solid obtained was dried in vacuo to remove any excess thiol and was recrystallized from ether/acetonitrile (2:1 v/v) to afford 1.96 g (43%) of pure product as white needles. $(Et_4N)(SPh)$ was prepared analogously and was recrystallized from THF/acetonitrile.

The complexes $[Fe(salen)L]^-$ were isolated as tetraethylammonium or sodium salts. Typical preparations for each are given; all operations were performed under a pure dinitrogen atmosphere with use of freshly degassed solvents. All compounds were isolated as purple to black, extremely dioxygen-sensitive, microcrystalline solids that are soluble in solvents such as acetonitrile, DMF, and acetone to form intense purple or purplish red solutions.

$(Et_4N)[Fe(salen)(SH)]$. To a stirred suspension of 0.50 g (1.55 mmol) of Fe(salen) in 80 mL of acetonitrile was added 0.25 g (1.60 mmol) of solid $(Et_4N)(SH)$. The reaction mixture immediately turned purple and was stirred for 3 h. The mixture was filtered, and the purple filtrate was concentrated in vacuo to about 20 mL. Ether (60 mL) was layered on top of the solution. Over a 12-h period a microcrystalline solid separated. Recrystallization of this material from ether/acetonitrile (2:1 v/v) afforded the pure product as 0.56 g (75%) of shiny purple microcrystals. Purified yields of other Et_4N^+ salts were 65–75%.

Na[Fe(salen)(S-2,4,6-*i*-$Pr_3C_6H_2$)]. To a stirred suspension of 0.64 g (2.00 mmol) of Fe(salen) in 40 mL of acetonitrile was added 0.52 g (2.02 mmol) of solid sodium 2,4,6-triisopropylbenzenethiolate. The mixture immediately assumed a purple color. After it was stirred for 12 h, the mixture was filtered, and the filtrate was concentrated at room temperature to about 15 mL. Ether (40 mL) was layered on top of the solution, causing precipitation of a microcrystalline solid over 12 h. This material was recrystallized from ether/acetonitrile (3:1 v/v), giving the pure product as 0.45 g (39%) of purple microcrystals. Purified yields of other sodium salts were 30–40%. In the purification of Na[Fe(salen)(S-$SiMe_3$)], the product was recrystallized from toluene/acetonitrile (4:1 v/v); in the presence of ether the Si–S bond was cleaved.

Listed in Table I are the members of the $[Fe(salen)L]^-$ class of complexes prepared and characterized in this work. Three compounds were analyzed in detail. All compounds were analyzed for Fe content. Determined values were within ±0.4% of calculated values.[31] In addition, all compounds were found to be pure by an ^1H NMR spectral criterion, and all exhibited isotropically shifted spectra characteristic of the class. A smaller number of $[Fe(X\text{-}salen)L]^-$ complexes were also prepared by the same procedure and used to confirm signal assignments of ring protons in the corresponding unsubstituted (X = H) species. These com-

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(31) See paragraph at the end of this article concerning supplementary material available.

Table I. Properties of [Fe(salen)L]$^-$ and [Fe(salen)L$_2$] Complexes in Acetonitrile Solutions (~25 °C)

$L^{-,0}$	salt	λ_{max}, nm (ϵ_M)	^{1}H NMR shifts, δ 3-H	4-H	5-H	6-H	$E_{1/2}$, V (ΔE_p, mV)
F$^-$	Et$_4$N$^+$	358 (11 500), 538 (1500)	−15.4	47.4	−7.2	38.6	−0.76 (60)
Cl$^-$	Et$_4$N$^+$	348 (11 500), 448 (sh, 1650), 482 (1900)	−17.6	57.4	−11.0	50.6	−0.35 (90)
OH$^-$	Et$_4$N$^+$	352 (12 000), 536 (1850)	−16.3	45.5	−6.5	41.0	−0.87
SCN$^-$	Et$_4$N$^+$	348 (11 500), 448 (sh, 1700), 484 (2000)	−24.4	58.4	−16.8	48.3	−0.22 (90)
CN$^-$	Et$_4$N$^+$	352 (12 000), 488 (2300), 524 (sh, 2100)	−24.7	57.7	−19.5	46.6	−0.31 (70)
p-MeC$_6$H$_4$O$^-$ [a]	Na$^+$	350 (8500), 534 (1000)	−17.5	55.4	−10.0	46.6	−0.73 (120)
			(−14.9, o-H; 10.7, m-H; 20.4, p-Me)				
SH$^-$	Et$_4$N$^+$	352 (11 000), 520 (2350), 572 (sh, 1950)	−18.4	55.4	−12.8	47.2	−0.67 (110)
EtS$^-$	Na$^+$	346 (12 500), 500 (2350), 564 (sh, 1850)	−17.8	50.0	−10.8	42.9 [b]	−0.68 (70)
t-BuS$^-$	Na$^+$	346 (11 000), 518 (1850), 580 (sh, 1350)	−18.0	50.6	−11.8	43.6	−0.69 (80)
			(16.9, t-Bu)				
Me$_3$SiS$^-$	Na$^+$	344 (9950), 510 (2400), 578 (sh, 1850)	−17.1	50.6	−9.5	44.6	−0.64 (110)
			(5.13, Me)				
PhS$^-$	Et$_4$N$^+$	340 (11 000), 512 (2400), 552 (sh, 2300)	−20.5	57.2	−15.6	47.4	−0.52 (60)
			(−22.7, o-H, p-H; 12.1, m-H)				
p-MeC$_6$H$_4$S$^-$	Et$_4$N$^+$	342 (11 500), 516 (2550), 556 (sh, 2450)	−20.5	57.4	−15.7	47.4	−0.54 (90)
			(−23.6, o-H; 12.6, m-H; 26.8, p-Me)				
2,6-Me$_2$C$_6$H$_3$S$^-$	Na$^+$	340 (11 000), 516 (2300), 568 (sh, 2000)	−19.5	53.5	−10.8	46.4	−0.54 (60)
			(32.5, o-Me; 18.5, m-H; −34.0, p-H)				
2,4,6-i-Pr$_3$C$_6$H$_2$S$^-$	Na$^+$	342 (12 000), 520 (2300), 568 (sh, 2050)	−18.7	54.3	−10.9	47.1	−0.54 (60)
			(3.8, o-CHMe_2; 16.6, o-CHMe$_2$; 13.5, m-H; −0.3, p-CHMe_2; 28.7, p-CHMe$_2$)				
DMF [c]		350 (12 000), 484 (sh, 2100), 508 (sh, 2100)	−15.4	57.4	−7.1	48.6 [c]	−0.27 (90)
DMF + py [d]		354, 474, 532 (sh)					−0.15 (90)

[a] Generated in situ by the reaction of equimolar Fe(salen) and Na(OC$_6$H$_4$-p-Me) in acetonitrile. [b] Ethyl signals not detected. [c] NMR in Me$_2$SO-d_6. [d] py:Fe(salen) = 200:1.

Table II. Summary of Crystal Data and Intensity Collection and Structure Refinement Parameters for (Et$_4$N)[Fe(5-NO$_2$salen)(S-p-tol)]

formula	C$_{31}$H$_{39}$FeO$_6$N$_5$S
mol wt	665.60
a, Å	9.644 (2)
b, Å	12.115 (3)
c, Å	14.788 (3)
α, deg	98.33 (2)
β, deg	105.84 (2)
γ, deg	98.41 (2)
cryst system	triclinic
Z	2
V, Å^3	1613.0 (6)
d_{obsd} [a] (d_{calcd}), g/cm^3	1.37 (1.37)
space group	$P\bar{1}$
cryst dimens, mm	0.32 × 0.40 × 0.60
radiation	Mo Kα (λ = 0.71069 Å)
abs coeff μ, cm^{-1}	5.76
scan speed, deg/min	2.0–29.3 (ω scan)
scan range, deg	0.6 below Kα_1 to 0.6 above Kα_2
bkgd/scan time ratio	0.25
2θ limits	$3° \leq 2\theta \leq 52°$
no. of data collected	8023 ($+h,\pm k,\pm l$)
no. of unique data ($F_o^2 > n\sigma(F_o^2)$)	3483 (n = 3.0)
no. of constraints	86
no. of variables	444
R_{merge} [b] (R_{iso}), %	2.04 (11.24)
R (R_w), % [c]	4.52 (6.15) [d]

[a] Determined by the neutral buoyancy in CCl$_4$/hexane. [b] $R_{merge} = \sum(N_i\sum_{j=1}^{N_i}(\bar{F}_i - F_j))/\sum(N_i\sum_{j=1}^{N_i}F_j)$, where N_i is the number of equivalent reflections merged to give the mean, $\bar{F}_i$, F_j is any one member of this set, and the calculations are done on a scale of F_o^2. [c] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o|^2 - |F_c|^2)/\sum w|F_o|^2]^{1/2}$. [d] Weighting scheme for least-squares refinement: $w = (F_o/P(1))^2$, $F_o \leq P(1)$; $w = (P(1)/F_o)^2$, $F_o > P(1)$; $P(1) = F(\min(|F_o|^2 - |F_c|^2)) = 16.0$.

plexes were judged to be adequately identified by their ^{1}H NMR spectra and were not analyzed. (Et$_4$N)[Fe(5-NO$_2$salen)(S-p-tol)], also characterized by its NMR spectrum, was prepared for use in electron-exchange studies and an X-ray structure determination.

(Et$_4$N)[Fe(salen)(S-p-tol)]. Anal. Calcd for C$_{31}$H$_{41}$FeN$_3$O$_2$S: C, 64.69; H, 7.18; Fe, 9.70; N, 7.30; S, 5.57. Found: C, 64.36; H, 7.21; Fe, 9.63; N, 7.12; S, 6.16.

Na[Fe(salen)(SEt)]. Anal. Calcd for C$_{18}$H$_{19}$FeN$_2$NaO$_2$S: C, 53.22; H, 4.68; Fe, 13.76; N, 6.90; Na, 5.67; S, 7.89. Found: C, 53.56; H, 4.41; Fe, 13.70; N, 6.96; Na, 5.86; S, 7.73.

(Et$_4$N)[Fe(salen)Cl]. Anal. Calcd for C$_{24}$H$_{34}$ClFeN$_3$O$_2$: C, 59.09; H, 7.02; Cl, 7.27; Fe, 11.45; N, 8.61. Found: C, 58.78; H, 7.30; Cl, 7.66; Fe, 11.30; N, 8.39.

Collection and Reduction of X-ray Data. Dark purple crystals of (Et$_4$N)[Fe(5-NO$_2$salen)(S-p-tol)] were obtained by layering ether on an acetonitrile solution and allowing the mixture to stand overnight. A suitable crystal was mounted in a glass capillary under dinitrogen, and the capillary was sealed. Diffraction data were collected on a Nicolet P3F four-circle automated diffractometer with use of graphite-monochromatized Mo Kα radiation. Unit cell parameters and the orientation matrix were obtained from 25 strong, machine-centered reflections ($20° \leq 2\theta \leq 25°$). Data collection and crystal parameters are contained in Table II. Three check reflections monitored every 123 reflections exhibited no significant decay over the entire period of data collection. Lorentz and polarization corrections were applied with the program XTAPE from the SHELXTL program package (Nicolet XRD Corp., Madison, WI). Examination of appropriate reflections indicated that an absorption correction was unnecessary. Axial photographs revealed no symmetry, and simple E statistics (MULTAN 80) favored the centrosymmetric space group $P\bar{1}$ (No. 2). Density measurements in conjunction with volume calculations suggested Z = 2. Successful solution and refinement confirmed the choice of space group.

Solution and Refinement of the Structure. Atom scattering factors were taken from a standard tabulation.[32] Nearly the entire anion and over half the cation atoms were located by direct methods (MULTAN 80) by using random groups. The structure was refined with use of CRYSTALS; phenyl rings and the cation were constrained by the method of additional observational equations.[33] Isotropic refinement of all nonhydrogen atoms with unit weights converged at 11.2%. In further refinements, all hydrogen atoms were included at 0.96 Å from, and with isotropic thermal parameters 1.2 times those of, bonded carbon atoms. A difference map after convergence showed four peaks in the region of the methylene carbon atoms of the cation, indicating disorder. Attempted modeling of the disorder with the occupancies of all methylene carbon atoms treated as equivalent refined to an occupancy ratio of 0.72/0.28. Owing to the large thermal parameters for the positions of lesser occupancy, these were refined isotropically and hydrogen atoms were not included. After a final full-matrix refinement, a difference map showed no peak >0.3 e/Å^3. The final agreement factors and a description of the weighting scheme can be found in Table II. Positional parameters are collected in Table III.[31]

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(32) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(33) Waser, J. *Acta Crystallogr.* **1963**, *16*, 1091.

Table III. Positional Parameters (×10^4) for (Et$_4$N)[Fe(5-NO$_2$salen)(S-*p*-tol)]

atom	*x/a*	*y/b*	*z/c*
		Anion	
Fe(1)	8107.3 (7)	4945.3 (5)	3622.7 (5)
O(11)	6945 (3)	5537 (2)	4442 (2)
C(12)	6837 (4)	6557 (3)	4784 (3)
C(11)	7764 (4)	7559 (3)	4719 (3)
C(16)	7549 (4)	8618 (3)	5094 (3)
C(15)	6474 (5)	8711 (3)	5535 (3)
C(14)	5566 (5)	7752 (3)	5611 (3)
C(13)	5742 (4)	6693 (3)	5245 (3)
N(11)	6299 (5)	9827 (3)	5933 (3)
O(12)	5353 (5)	9892 (3)	6347 (3)
O(13)	7092 (5)	10664 (3)	5850 (3)
C(17)	8952 (5)	7544 (3)	4297 (3)
N(12)	9241 (4)	6640 (3)	3881 (3)
C(18)	10477 (6)	6751 (4)	3476 (4)
C(28)	11306 (5)	5819 (4)	3735 (4)
N(22)	10254 (4)	4748 (3)	3540 (3)
C(27)	10630 (5)	3812 (4)	3288 (3)
C(21)	9776 (4)	2690 (3)	3202 (3)
C(22)	8523 (4)	2518 (3)	3536 (3)
O(21)	7925 (3)	3332 (2)	3827 (2)
C(23)	7892 (5)	1381 (4)	3530 (4)
C(24)	8418 (5)	481 (4)	3165 (3)
C(25)	9603 (5)	676 (3)	2803 (3)
C(26)	10301 (5)	1764 (3)	2842 (3)
N(21)	10130 (5)	−280 (4)	2404 (3)
O(22)	11239 (5)	−94 (3)	2142 (3)
O(23)	9442 (5)	−1239 (3)	2324 (3)
S(1)	6829 (1)	4939 (1)	1993.6 (9)
C(31)	5189 (4)	3889 (3)	1554 (3)
C(36)	4207 (5)	3869 (4)	670 (3)
C(35)	2993 (5)	3002 (4)	258 (3)
C(34)	2705 (5)	2119 (4)	720 (3)
C(33)	3654 (5)	2149 (4)	1615 (3)
C(32)	4871 (5)	3018 (4)	2030 (3)
C(37)	1422 (6)	1142 (5)	253 (4)
		Cation	
N(41)	3256 (6)	7503 (5)	1073 (3)
C(41)	4484 (10)	6981 (8)	1598 (5)
C(42)	4800 (10)	7318 (7)	2703 (5)
C(43)	3061 (11)	7077 (10)	4 (5)
C(44)	1873 (14)	7547 (12)	−646 (5)
C(45)	1870 (13)	7217 (11)	1344 (7)
C(46)	1335 (16)	5921 (14)	1116 (10)
C(47)	3700 (14)	8791 (10)	1327 (7)
C(48)	5040 (16)	9262 (9)	1117 (8)
C(51)	3314 (20)	7672 (20)	2163 (16)
C(53)	1896 (43)	7808 (42)	418 (18)
C(55)	2799 (34)	6157 (30)	871 (33)
C(57)	4732 (46)	7970 (19)	936 (40)

Other Physical Measurements. All measurements were made at ambient temperature under anaerobic conditions; solvents were thoroughly degassed prior to use. Absorption spectra were recorded on a Cary Model 219 spectrophotometer. ^{1}H NMR spectra were determined with use of a Bruker AM 250 spectrometer; chemical shifts are referenced to Me$_4$Si internal standard. The magnetic susceptibility determination of a polycrystalline solid was performed with an SHE 905 SQUID magnetometer operating between 6 and 300 K. Solution measurements were made by the usual NMR method; the susceptibility of acetonitrile solvent was a literature value.[34] Electrochemical measurements were performed with standard PAR instrumentation, a glassy-carbon working electrode, and 0.1 M (n-Bu$_4$N)(ClO$_4$) supporting electrolyte; potentials are referenced to the SCE. In addition to the potentials in acetonitrile solutions listed in Table I, the following values of $E_{1/2}$ (ΔE_p, mV) in acetone vs SCE for Et$_4$N$^+$ salts were utilized in a study of electron-transfer reactions: [Fe(salen)Cl]$^{0,-}$, −0.39 V (120); [Fe(salen)NCS]$^{0,-}$, −0.21 V (80); [Fe(salen)(S-*p*-tol)]$^{0,-}$, −0.53 V (120); [Fe(3-*t*-Busalen)(S-*p*-tol)]$^{0,-}$, −0.66 (70), [Fe(5-*t*-Busalen)(S-*p*-tol)]$^{0,-}$, −0.54 V (120); [Fe(5-*t*-Busalen)Cl]$^{0,-}$, −0.40 V (100); [Fe(5-NO$_2$salen)(S-*p*-tol)]$^{0,-}$, −0.21 V (120); [Fe(5-NO$_2$salen)Cl]$^{0,-}$, −0.08 V (90).

Electron-Transfer Reactions. These reactions between Fe(II) and Fe(III) salen complexes were examined by ^{1}H NMR spectroscopy. A typical experiment was performed as follows under strictly anaerobic conditions. A 14.1 mM solution of (Et$_4$N)[Fe(salen)Cl] was prepared in 1 mL of acetone-d_6. To a 0.77-mL aliquot was added 3.88 mg of Fe(salen)Cl, resulting in equimolar quantities of the two complexes at the start of the reaction. The system was allowed to react until all solid had dissolved (30–60 min). The solution was filtered into a 5-mm NMR tube, and the spectrum was recorded within 30 min.

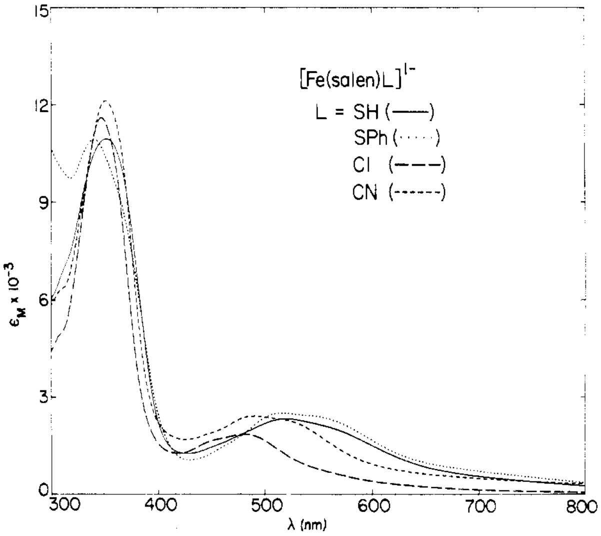

Figure 1. UV/visible absorption spectra of a series of Et$_4$N$^+$ salts of [Fe(salen)L]$^-$ complexes (L = SH$^-$, SPh$^-$, Cl$^-$, CN$^-$) in acetonitrile solutions.

Results and Discussion

Preparation and Properties of Compounds. A new class of salen complexes has been prepared by the heterogeneous reaction (1) in acetonitrile. Products were isolated as sodium or tetraethylammonium salts; those obtained in substance are given in Table I; ligands L range from hard (halide, hydroxide) to soft (thiolate). Even the relatively hindered ligand 2,4,6-triisopropylbenzenethiolate binds readily. No X-ray structure is available for the precursor complex Fe(salen). However, its sparing solubility in all but the most strongly coordinating solvents indicates that it is oligomeric in the solid state. Reaction 1, therefore, involves the cleavage of bridges of the Fe(II)–phenolate–Fe(II) type. The related complex Fe(acen) is dimeric in the solid state with presumably analogous Fe–(OR)$_2$–Fe bridges between six-coordinate Fe(II) atoms.[35] The stabilization of sodium salts doubtless involves the interaction of Na$^+$ with the phenolate oxygen atoms, a bonding mode abundantly demonstrated in salen and related complexes.[17,36] These salts are readily soluble in acetonitrile.

$$\mathrm{Fe(salen)} + (\mathrm{Na^+/Et_4N^+})\mathrm{L^-} \xrightarrow{\mathrm{MeCN}} (\mathrm{Na^+/Et_4N^+})[\mathrm{Fe(salen)L}] \quad (1)$$

Of the solvents tested, Et$_4$N$^+$ salts are freely soluble in DMF and acetonitrile and somewhat less soluble in acetone. In acetonitrile solutions they display colors ranging from deep purple to purplish red[37] as redox potentials become less negative (Table

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(34) Gerger, W.; Mayer, U.; Gutmann, V. *Monatsh. Chem.* **1977**, *108*, 417.

(35) Corazza, F.; Floriani, C.; Zehnder, M. *J. Chem. Soc., Dalton Trans.* **1987**, 709. (acen = *N*,*N'*-ethylenebis(acetylacetone iminato)(2−).)

(36) (a) Floriani, C.; Calderazzo, F. *J. Chem. Soc., Chem. Commun.* **1973**, 384. (b) Milburn, H.; Truter, M. R.; Vickery, B. L. *J. Chem. Soc., Dalton Trans.* **1974**, 841. (c) Bresciani-Pehor, N.; Calligaris, M.; Delise, P.; Nardin, G.; Randaccio, L.; Zotti, E.; Fachinetti, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1976**, 2310. (d) Armstrong, L. G.; Lip, H. C.; Lindoy, L. F.; McPartlin, M.; Tasker, P. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1771. (e) Fachinetti, G.; Floriani, C.; Zanazzi, P. F.; Zanzari, A. R. *Inorg. Chem.* **1978**, *17*, 3002. (f) Pasquali, M.; Marchetti, F.; Floriani, C.; Cesari, M. *Inorg. Chem.* **1980**, *19*, 1198. (g) Corazza, F.; Floriani, C.; Zehnder, M. *J. Chem. Soc., Chem. Commun.* **1986**, 1270. (h) Arena, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1986**, 1369.

(37) The only exception is [Fe(5-NO$_2$salen)(S-*p*-tol)]$^-$, which is blackish green in solution.

I). Solutions using these solvents are entirely stable in the absence of dioxygen; in its presence, the Fe(II) complexes are rapidly converted to [Fe(salen)]$_2$O. In chlorinated solvents under anaerobic conditions, the complexes are slowly transformed to Fe(salen)Cl.

In solution, [Fe(salen)L]$^-$ complexes are most readily recognized by their characteristic LMCT absorption spectra, which are quite sensitive to the nature of L. Representative spectra are shown in Figure 1; these consist of two poorly resolved bands in the visible and a much more intense band in the ultraviolet region near 350 nm. These species also display in cyclic voltammetry in acetonitrile or acetone solutions a single, chemically reversible redox couple (2). The majority of potentials are relatively negative, indicating

$$\mathrm{Fe(salen)L} + e^- \rightleftharpoons [\mathrm{Fe(salen)L}]^- \qquad (2)$$

$$2\mathrm{Fe(salen)(SR)} \rightarrow 2\mathrm{Fe(salen)(solv)_2} + \mathrm{RSSR} \qquad (3)$$

ready oxidation of the monoanion. There is no general correlation of absorption band maxima and potentials.

Iron(III) thiolate complexes with R = H, Et, *t*-Bu, and Me$_3$Si autoreduce by means of reaction 3 and proved too unstable to isolate. However, Fe(salen)(SPh) can be isolated.[30] In a typical experiment to examine stability, potential sweep through the redox couple [Fe(salen)(SEt)]$^{0/-}$ at scan rates of 50–200 mV revealed reversible charge transfer with $E_{1/2} = -0.68$ V; no other redox process was observed. In addition to this couple, subsequent scans showed the features $E_{pc} = -0.76$ V and $E_{1/2} = -0.32$ V, corresponding to the irreversible reduction of EtSSEt and the reversible couple [Fe(salen)(MeCN)$_2$]$^{+/0}$ (disolvate assumed), respectively. A final solution property of importance is found in the moderately well-resolved, isotropically shifted ^{1}H NMR spectra considered below, in which the shifts are extremely sensitive to L. Given the large number of examples, the spectral patterns are clearly diagnostic of the [Fe(salen)L]$^-$ complex type. The absorption and ^{1}H NMR spectra ensure that reaction 1 with L = *p*-cresolate in situ affords [Fe(salen)(OC$_6$H$_4$-*p*-Me)]$^-$, whose Na$^+$ or Et$_4$N$^+$ salt we were unable to isolate in pure form. It is likely that this reaction can be extended to a wider variety of ligands than examined here.

Magnetism. On the basis of its solution properties, [Fe(salen)(S-*p*-tol)]$^-$ is a typical member of the set. The magnetism of its polycrystalline Et$_4$N$^+$ salt was investigated at 7–300 K to define the ground-state spin and allow structural inferences. The compound follows the Curie–Weiss law (4) with the indicated pa-

$$\chi^M = C/(T + \Theta) \qquad (4)$$

$$C = 3.127 \pm 0.006 \text{ emu K/mol}$$

$$\Theta = 0.11 \pm 0.26 \text{ K}$$

$$\mu_{\text{eff}} = 4.99\ \mu_B$$

rameters.[38] The Curie constant is in good agreement with that for a $S = 2$ ground state ($C = 3$ when $g = 2$). The absence of magnetic coupling strongly suggests a mononuclear structure, as confirmed for a related complex by X-ray analysis (vide infra). In acetonitrile solution at 298 K, the same compound gives $\mu_{\text{eff}} = 4.94\ \mu_B$, in excellent agreement with the solid-state magnetic moment. Given this result and their similarities of isotropic shifts, we conclude that all [Fe(salen)L]$^-$ complexes have quintet spin states and mononuclear five-coordinate structures in solution. In this event, two complexes provide infrequent examples of terminal Fe^{II}–OH and Fe^{II}–SH groups. Further, under the empirical infrared criteria for thiocyanate–metal coordination,[39] $\nu_{CN} = 2060$ cm^{-1} (mull) and 2078 cm^{-1} (acetonitrile) for [Fe(salen)(NCS)]$^-$ indicate Fe–NCS bonding. For Fe(salen)(NCS) the corresponding band appears at 2050 cm^{-1} (mull).[7]

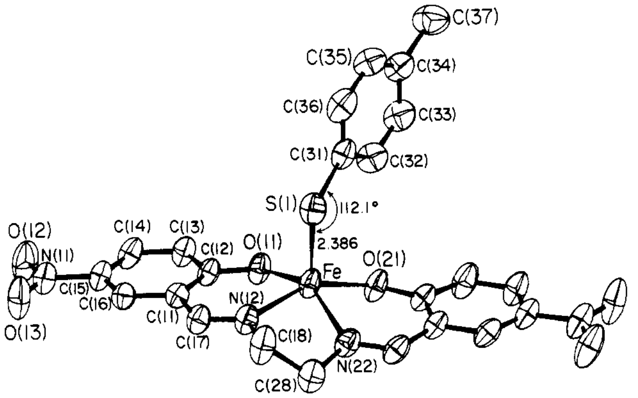

Figure 2. Structure of [Fe(5-NO$_2$salen)(S-*p*-tol)]$^-$ as its Et$_4$N$^+$ salt, showing atom-labeling scheme and 50% probability ellipsoids. Ring 2 (right) is numbered analogously to ring 1.

Table IV. Selected Interatomic Distances (Å), Angles (deg), and Other Structural Data for [Fe(5-NO$_2$salen)(S-*p*-tol)]$^-$

Fe–O(11)	1.989 (3)	Fe–N(12)	2.111 (4)
Fe–O(21)	2.011 (3)	Fe–N(22)	2.153 (4)
Fe–S(1)	2.386 (2)	S(1)–C(31)	1.777 (5)
S(1)–Fe–O(11)	108.3 (1)	O(11)–Fe–O(21)	99.7 (1)
S(1)–Fe–O(21)	108.8 (1)	O(11)–Fe–N(12)	86.1 (1)
S(1)–Fe–N(12)	94.0 (1)	O(21)–Fe–N(22)	84.0 (1)
S(1)–Fe–N(22)	101.9 (1)	N(12)–Fe–N(22)	77.1 (1)
O(11)–Fe–N(22)	146.3 (1)	O(21)–Fe–N(12)	153.0 (1)
Fe–O(11)–C(12)	132.7 (3)	Fe–N(12)–C(17)	128.7 (3)
Fe–O(21)–C(22)	130.6 (3)	Fe–N(22)–C(27)	126.0 (3)
Fe–N(12)–C(18)	112.7 (3)	Fe–N(22)–C(28)	114.4 (3)
Fe–S(1)–C(31)	112.1 (1)		

C(31)–S(1)–Fe–O(11)	–69.95
C(31)–S(1)–Fe–O(21)	37.40
C(36)–C(31)–S(1)–Fe	171.0
C(32)–C(31)–S(1)–Fe	–13.5

displacements from O(11,12)N(12,22) mean plane: O(11), –0.07; O(21), +0.07; N(12), +0.08; N(22), –0.08; Fe, +0.49

Structure of [Fe(5-NO$_2$salen)(S-*p*-tol)]$^-$. The five-coordinate structure referred to above has been established by X-ray diffraction for this complex, which is representative of the [Fe(salen)L]$^-$ class. The structure is shown in Figure 2; selected metric data are contained in Table IV. It is one of three known structures of an Fe(II)–salen complex, the others being trigonal bipyramidal with one ligand furnished by the bridge portions of pentadentate ligands.[23,24] The stereochemistry of [Fe(5-NO$_2$salen)(S-*p*-tol)]$^-$ is that of a somewhat distorted square pyramid with the sulfur atom occupying the axial position. The O$_2$N$_2$ base of the pyramid is nonplanar with atom displacements of ±0.07–0.08 Å from the unweighted-least-squares plane. The Fe atom is 0.49 Å above this plane. The Schiff base ligand adopts the umbrella conformation often observed in, but not as pronounced as for some, salen complexes.[40] As measured by the dihedral angles between the mean O$_2$N$_2$ plane and those of the two salicylideneamino portions, $\alpha = 11.0°$ and $\beta = 6.4°$. The phenyl ring of the axial substituent is positioned about 16° from the plane that bisects the O–Fe–O and N–Fe–N angles in the direction of O(21), and it is twisted by 8° from being perpendicular to the O$_2$N$_2$ mean plane.

The Fe–O and Fe–N bond distances in the present complex appear to be 0.02–0.05 Å longer than in trigonal-bipyramidal Fe(II) salen complexes.[23,24] When compared to those of [Fe(salen)]$_2$S[18] and a substituted derivative[19] with axial sulfur (μ_2-S) ligands in square-pyramidal coordination, Fe–N bond distances are nearly the same but Fe–O distances are 0.06–0.11 Å shorter. This reveals that the size difference between high-spin Fe(II) and Fe(III) is mainly manifested in bonds between charged atoms. The Fe–S distance of 2.386 (2) Å is at the long end of a 2.33–2.39-Å range of Fe(II)–SR bond lengths established for porphyrin

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(38) Correlation coefficient $r = 0.99996$.

(39) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley-Interscience: New York, 1986; pp 283–287.

(40) Calligaris, M.; Nardin, G.; Randaccio, L. *Coord. Chem. Rev.* **1972**, *7*, 385.

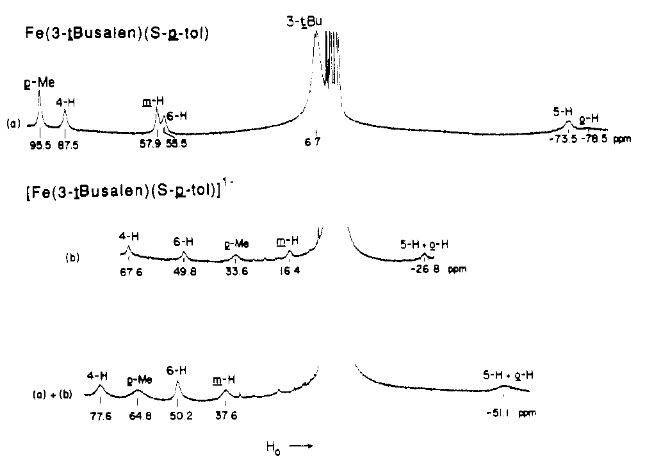
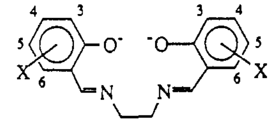


Figure 3. ^{1}H NMR spectra of [Fe(3-*t*-Busalen)(S-*p*-tol)]$^{0,-}$ and a reaction mixture 10 mM in each complex, illustrating chemical shift averaging from electron self-exchange. In this and subsequent spectra, the solvent is acetone-d_6, the temperature is 297 K, shifts and signal assignments are indicated, and an intense portion of the diamagnetic region of the spectrum containing primarily solvent and cation resonances has been excised (no paramagnetically shifted resonances are located in this region).

complexes with five- and six-coordination by X-ray diffraction[41-43] and Fe EXAFS.[44] It is also somewhat longer than the mean value (2.34 (1) Å) in a trigonal-bipyramidal complex derived from the dithiolate analogue of salen.[45] The out-of-plane displacement of the Fe atom is comparable to the values for high-spin five-coordinate [Fe(TPP)(SEt)]$^-$[41] (0.52 Å) and [Fe(TpivPP)(SC$_6$HF$_4$)]$^-$[42] (0.42 Å). To the extent that these comparisons are valid, [Fe(5-NO$_2$salen)(S-*p*-tol)]$^-$ adopts a conventional structure with no destabilizing features except for perhaps a slightly lengthened axial bond.

Electron-Transfer Reactions and Mechanism. Initial comparison of published examples of isotropically shifted ^{1}H NMR spectra of Fe(salen)L complexes[5,9,10] with the chemical shift data in Table I for complexes with similar ligands or the same axial ligand made evident that Fe(III) ($S = {}^5/_2$) and Fe(II) ($S = 2$) complexes could be distinguished under conditions of slow electron exchange. Further, spectra of both types of complexes give isotropically shifted patterns of resonances fully consistent with ligand → metal antiparallel spin delocalization.[5,46] Under this delocalization mode, 3-H and 5-H isotropic shifts are positive and 4-H and 6-H isotropic shifts are negative; the ligand numbering scheme is as follows:



Thereafter, we established that in ca. 10 mM acetone solutions the systems Fe(salen)Cl/[Fe(salen)Cl]$^-$ at 220–320 K and Fe(salen)(SR)/[Fe(salen)(SR)]$^-$ (R = *p*-tol) at 297 K underwent fast electron self-exchange, as manifested by exchange-broadened spectra with averaged chemical shifts. Shown in Figure 3 are typical spectra of [Fe(salen)L]$^{0,-}$ complexes and the spectrum of an equimolar equilibrium solution of the latter self-exchange system in acetone. Chemical shifts agree to within a few percent of those calculated from the shifts of the separate components. The 3-H and 5-H resonances are broadened to the largest extent and are the least useful in the systems that follow.

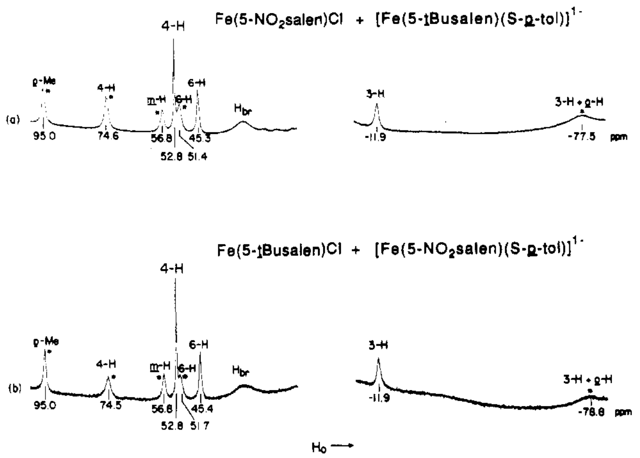


Figure 4. ^{1}H NMR spectra of equimolar reaction systems containing initially Fe(5-NO$_2$salen)Cl + [Fe(5-*t*-Busalen)(S-*p*-tol)]$^-$ (top) and Fe(5-*t*-Busalen)Cl + [Fe(5-NO$_2$salen)(S-*p*-tol)]$^-$ (bottom): (br) CH$_2$CH$_2$ (salen); (*) Fe(III) signal.

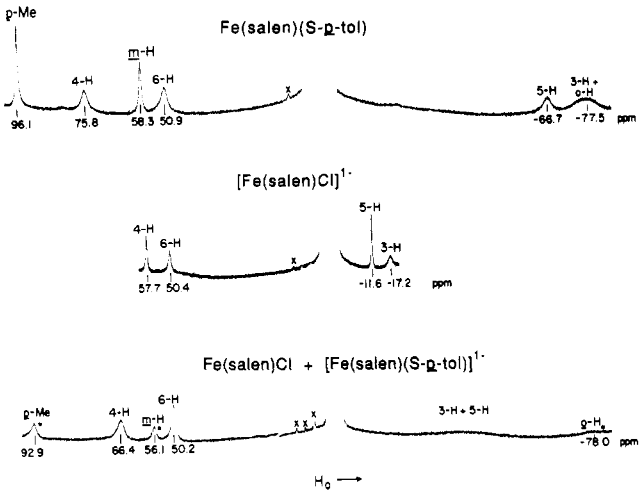


Figure 5. ^{1}H NMR spectra of Fe(salen)(S-*p*-tol), [Fe(salen)Cl]$^-$, and an equimolar reaction system of the two complexes: (×) impurity; (*) Fe(III) signal.

We have examined the generalized reaction (5), all components of which are high-spin, in terms of four specific cases, reactions 6–9 (R = *p*-tol). These have been selected in an attempt to

$$\mathrm{Fe(X\text{-}salen)L} + [\mathrm{Fe(X'\text{-}salen)L'}]^- \rightarrow [\mathrm{Fe(X\text{-}salen)L/L'}]^- + \mathrm{Fe(X'\text{-}salen)L'/L} \quad (5)$$

$$\mathrm{Fe(5\text{-}NO_2salen)Cl} + [\mathrm{Fe(5\text{-}\mathit{t}\text{-}Busalen)(SR)}]^- \rightarrow [\mathrm{Fe(5\text{-}NO_2salen)Cl}]^- + \mathrm{Fe(5\text{-}\mathit{t}\text{-}Busalen)(SR)} \quad (6)$$

$$\mathrm{Fe(5\text{-}\mathit{t}\text{-}Busalen)Cl} + [\mathrm{Fe(5\text{-}NO_2salen)(SR)}]^- \rightarrow [\mathrm{Fe(5\text{-}NO_2salen)Cl}]^- + \mathrm{Fe(5\text{-}\mathit{t}\text{-}Busalen)(SR)} \quad (7)$$

$$\mathrm{Fe(salen)Cl} + [\mathrm{Fe(salen)(SR)}]^- \rightarrow [\mathrm{Fe(salen)Cl}]^- + \mathrm{Fe(salen)(SR)} \quad (8)$$

$$\mathrm{Fe(salen)(NCS)} + [\mathrm{Fe(salen)(SR)}]^- \rightarrow [\mathrm{Fe(salen)(NCS)}]^- + \mathrm{Fe(salen)(SR)} \quad (9)$$

determine the mechanism of electron transfer. The notation of reaction 5 indicates the possibility of electron transfer occurring without or with axial ligand exchange.

Variations of axial ligand L and ring substituent X allow manipulation of the electrochemical driving force for electron

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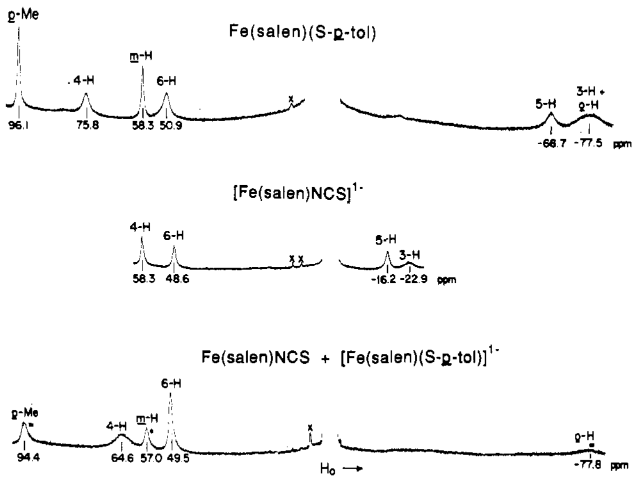

Figure 6. ^1H NMR spectra of Fe(salen)(S-*p*-tol), $[Fe(salen)(NCS)]^-$, and an equimolar reaction system of the two complexes: (×) impurity; (*) Fe(III) signal.

transfer. The spectra of Figure 4 demonstrate that the outcomes of reactions 6 and 7 are identical. Reaction 6 possesses a huge driving force for electron transfer ($E° = +0.46$ V, $K_{eq} = 6.3 \times 10^7$), which is the observed process. These and similar data refer to 297 K. For reaction 7, electron transfer is thermodynamically unfavorable ($E° = -0.19$ V, $K_{eq} = 6.0 \times 10^{-4}$) and the most stable products arise from axial ligand exchange. This reaction proceeds fully to the right. The results point out that the mechanisms for these reactions, if they are the same, must be conducive to both electron transfer and ligand substitution.

The spectrum of the products of reaction 8, whose components have identical salen ligands, is shown in Figure 5. Thiolate shifts are very close to the values for Fe(salen)(SR), whose spectrum is shown. Note that the *m*-H and *p*-Me shifts of $[Fe(salen)(SR)]^-$ are ca. 45 and 70 ppm, respectively, upfield from those of Fe(salen)(SR). Formation of the Fe(III) thiolate complex is expected, since electron transfer is downhill ($E° = +0.14$ V, $K_{eq} = 2.4 \times 10^2$). It is also observed that the salen 4-H resonances of the reactants are averaged to 66.4 ppm vs 66.7 ppm calculated for the equimolar reaction mixture. In reaction 9, whose product spectrum is provided in Figure 6, it is clear from the *p*-toluenethiolate shifts that $[Fe(salen)(SR)]^-$ is oxidized to Fe(salen)(SR), consistent with $E° = +0.32$ V and $K_{eq} = 2.7 \times 10^5$. Again, the salen resonances are averaged in the process, but the averaging may not be quite complete inasmuch as the broad 4-H signal is found at about 65 ppm vs 67.1 ppm, calculated for fast exchange.

In terms of final products, reaction 6 is one of electron transfer only, while reaction 7 is one of ligand exchange only and shows the preference of Fe(III) for an axial thiolate ligand. Reactions 8 and 9 are ones of electron transfer only but involve the averaging of salen protons over an Fe(II) and Fe(III) environment. These points are accounted for by the proposed mechanism in Figure 7. Here, reactants Fe(salen)L and $[Fe(salen)L']^-$ are chosen appropriately so that electron transfer is thermodynamically favored. These species form a doubly bridged intermediate with concomitant irreversible transfer of an electron. The intermediate can reversibly dissociate to final products Fe(salen)L′ and $[Fe(salen)L']^-$ and re-form, all the while undergoing ligand and electron exchange that approaches or achieves the NMR fast-exchange limit. The proposed intermediate requires the salen ligand to adopt a nonplanar conformation, among which the cis-*β* arrangement[47] is probable. It has been crystallographically confirmed for three Fe^{III}(salen)(bidentate) cases,[17] and other stable complexes of this type have been isolated.[48] When equimolar quantities of the products of reactions 8 and 9 were combined, ^1H NMR spectra identical with those afforded by the forward reaction systems were obtained. This result is fully consistent with the scheme in Figure 7.

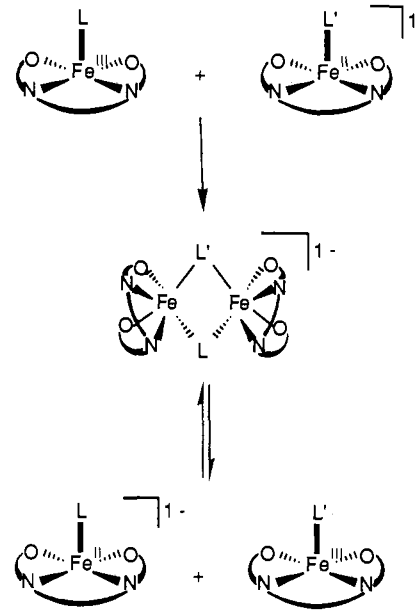

Figure 7. Mechanistic proposal for the reactions of electron transfer and axial ligand exchange between Fe(salen)L and $[Fe(salen)L']^-$ complexes. The proposed intermediate is depicted with the ligand in the cis-*β* configuration. The salen ligands may be the same (as shown) or different, as in reactions 6 and 7.

Another mechanistic pathway consistent with the NMR results involves axial ligand dissociation. We consider such a pathway, which implicates *discrete* ligand anions, to be improbable in the weakly polar medium provided by the acetone solvent used for reactions 6–9. Ligand dissociation of an Fe(III) complex would produce separated ions, a possibility that we discount. Ligand dissociation of an Fe(II) complex is somewhat more probable. But it should be noted that in reactions 6–9 the Fe(II) reactant carries the rather basic *p*-toluenethiolate axial ligand, whose generation in acetone would appear far less likely than dissociation of a very weakly basic ligand such as chloride. If a dissociative mechanism involving Fe(II) is pursued, the only difference between it and the scheme in Figure 7 is the formation of an intermediate with one bridging ligand. Other descriptions involving intermediates as tight ion pairs or cage entities, generated by axial ligand dissociation, are merely different conceptions of the same essential mechanism. We consider that the proposed mechanism provides additional insight into the pathway(s) by which coordinatively unsaturated complexes of the general type studied may undergo electron transfer and ligand exchange.

Summary. This research has resulted in the recognition and characterization of a new class of Fe–salen complexes. Its members $[Fe(salen)L]^-$ bind a variety of axial ligands L^-, contain high-spin Fe(II) in square-pyramidal coordination, exhibit isotropically shifted ^1H NMR spectra of good resolution, and are oxidizable to Fe(salen)L in electrochemically reversible processes.[49] A feasible mechanism has been deduced for electron transfer and ligand exchange, involving a doubly bridged binuclear intermediate. Finally, the ready formation of $[Fe(salen)(OC_6H_4\text{-}p\text{-}Me)]^-$ does not sustain the contention of Pyrz et al.[10] that phenolates as axial ligands are not likely to have a high affinity for Fe(salen). As already observed, this complex has good affinity for both soft and hard anionic axial ligands including, presumably, the phenolate atom in another molecule of Fe(salen) in the solid state.

Acknowledgment. This research was supported by NIH Grant GM 28856. X-ray diffraction equipment was obtained by NIH Grant 1 S10 RR 02247.

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(49) Note that another oxidation state, Fe(I), can also be achieved in the form of $[Fe(salen)]^-$ in THF solution.[6a]

Registry No. (Et$_4$N)[Fe(salen)(SH)], 114324-79-7; Na[Fe(salen)(EtS)], 114324-80-0; Na[Fe(salen)(*t*-BuS)], 114324-81-1; Na[Fe(salen)(Me$_3$SiS)], 114324-82-2; (Et$_4$N)[Fe(salen)(PhS)], 114324-84-4; (Et$_4$N)[Fe(salen)(*p*-MeC$_6$H$_4$S)], 114324-86-6; Na[Fe(salen)(2,6-Me$_2$C$_6$H$_3$S)], 114324-87-7; Na[Fe(salen)(2,4,6-Me$_3$C$_6$H$_2$S)], 114324-88-8; (Et$_4$N)[Fe(salen)Cl], 114324-90-2; (Et$_4$N)[Fe(salen)F], 114324-92-4; (Et$_4$N)[Fe(salen)(CN)], 114324-94-6; (Et$_4$N)[Fe(salen)(NCS)], 114324-96-8; (Et$_4$N)[Fe(salen)(OH)], 114324-98-0; Na[Fe(salen)(*p*-MeC$_6$H$_4$O)], 114324-99-1; Fe(salen)(DMF)$_2$, 114325-00-7; Fe(salen)(py)$_2$, 54477-48-4; Fe(3-*t*-Busalen)Cl, 114325-01-8; Fe(5-*t*-Busalen)Cl, 114325-02-9; Fe(5-NO$_2$salen)Cl, 62945-13-5; Fe(3-*t*-Busalen)(S-*p*-tol), 114325-03-0; Fe(5-*t*-Busalen)(S-*p*-tol), 114325-04-1; (Et$_4$N)[Fe(5-NO$_2$salen)(S-*p*-tol)], 114325-06-3; [Fe(3-*t*-Busalen)(S-*p*-tol)]$^-$, 114325-07-4; [Fe(5-NO$_2$salen)(S-*p*-tol)]$^-$, 114325-05-2; Fe(salen)(S-*p*-tol), 81276-94-0; (Et$_4$N)(SPh), 3193-72-4; (Et$_4$N)(S-*p*-tol), 76750-18-0; HS-*p*-tol, 106-45-6; HSPh, 108-98-5; Fe(salen), 14167-12-5.

Supplementary Material Available: A table of iron analyses for compounds in Table I and crystallographic data for (Et$_4$N)[Fe(5-NO$_2$salen)(S-*p*-tol)], including tabulations of positional and thermal parameters, interatomic distances and angles, and calculated hydrogen atom positions (6 pages); a table of calculated and observed structure factors (22 pages). Ordering information is given on any current masthead page.

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Relationship between Structural Change and Heterogeneous Electron-Transfer Rate Constant in Iron–Tetraphenylporphyrin Complexes

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Received December 11, 1987

The rate of metal-centered electrochemical reduction is reported for six high-spin iron(III)–tetraphenylporphyrin (TPP) complexes, Fe(TPP)X (X = Br$^-$, Cl$^-$, F$^-$, C$_6$H$_5$O$^-$, CH$_3$O$^-$, CH$_3$CO$_2^-$), three low-spin iron(III) complexes, Fe(TPP)X$_2$ (X = pyridine, imidazole, CN$^-$), and a manganese(III) complex, Mn(TPP)Cl, in CH$_2$Cl$_2$. Heterogeneous electron-transfer rate constants (k_s^{app}) are smaller by 0.3–1.3 orders of magnitude for high-spin Fe(TPP)X and Mn(TPP)Cl reductions compared with those for low-spin Fe(TPP)X$_2$ reductions. These differences result from the greater changes in molecular structure that accompany reduction of the high-spin species and correspond to increases in the inner-shell activation energy, $\Delta(\Delta G^*_{is})$, of up to 1300 cal mol^{-1}. We have quantitatively correlated relative rate constants for Fe(TPP)X and Mn(TPP)Cl reductions with porphyrin structural data using the Marcus theory. The diminished rate of Mn(TPP)Cl charge transfer derives exclusively from the large increase (0.37 Å) in metal out-of-plane displacement that accompanies reduction of Mn(TPP)Cl to [Mn(TPP)Cl]$^-$; no change occurs in the axial Mn–Cl dimension. High-spin Fe(TPP)X reductions are accompanied by increases in both the metal out-of-plane distance and axial Fe–X bond length. The latter term is the predominant contributor to $\Delta(\Delta G^*_{is})$; thus, k_s^{app} for Fe(TPP)X reduction decreases systematically as the frequency of the Fe–X vibration increases.

Introduction

Iron porphyrins are important model compounds for hemoproteins.[2,3] There is considerable interest in the electrochemistry of these complexes[4] as a guide to understanding the electron-transfer behavior of heme centers in naturally occurring systems. Electrochemical studies commonly have addressed the influence of porphyrin structure and axial ligation on half-wave potentials[5] and the stoichiometry[6] of electrode half-reactions. These relationships are reasonably well understood. The same structural features influence the kinetics of metal-centered electron-transfer reactions of porphyrins.[7-13] Generally, it is true that electron transfers involving high-spin/high-spin or high-spin/low-spin couples are slower than those involving low-spin species exclusively. However, specific factors underlying the dependence of electron transfer rate on porphyrin structure and spin state remain poorly understood.

High-spin ($S = {}^5/_2$) iron(III) porphyrins, Fe(P)X, typically are five-coordinate species with the iron atom displaced substantially out of the plane toward the axial ligand, X. Low-spin ($S = 1/2$) iron(III) porphyrins, Fe(P)X$_2$, are six-coordinate; the two axial ligands constrain the metal to lie essentially in the porphyrin plane. In the latter case, reduction proceeds to six-coordinate iron(II) (low spin, $S = 0$) with little structural change and a relatively rapid rate of electron transfer. The slow electron-transfer rates associated with reduction of high-spin iron(III) porphyrins generally are attributed to greater activation energy barriers arising from elongation or cleavage of the axial Fe–X bond or to movement of the Fe atom with respect to the porphyrin plane. The influence of axial ligand character on electron-transfer rate at a metal–porphyrin center has been investigated in several instances,[9,12,13] but a satisfactory correlation of these parameters has not been achieved.

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