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Iron(III) Nitrate Complexes with Linear Pentacoordinate Ligands and their Base Hydrolysis Products

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Abstract

The complexes, Fe(saldpt)NO_3, [Fe(salmedpt)]$_2$-(NO_3)(OH), Fe(saldien)NO_3, and Fe(salmedien)$NO_3 \cdot CH_2Cl_2$, have been prepared. Solid state properties (IR spectra, Mössbauer spectra and magnetic moments) and solution properties (electronic spectra, PMR spectra, conductivities and cyclic voltammograms) have been measured. The saldpt and saldien compounds when reacted with aqueous KOH formed Fe(saldpt)sal and Fe(saldien)$OC_2H_5 \cdot H_2O$. Single crystals of Fe(saldpt)sal were prepared and examined. Crystal data: Fe(saldpt)sal: monoclinic, space group $P2_1/c$(#14), $a = 12.486(5)$, $b = 18.502(8)$, $c = 10.870(5)$ Å, $\beta = 104.23(3)°$, $V = 2434(2)$ Å^3, $Z = 4$, $D_c = 1.40$ g cm^{-3}, $R = 0.0473$ ($R_w = 0.0681$) for 317 parameters and 2107 data with $F_o^2 > 3\sigma(F_o^2)$.

Introduction**

Metal complexes with pentadentate ligands are relatively uncommon. Only about seven different metal ions have been investigated bound to either saldpt or saldien or their derivatives [1–8]. These linear, dianionic, Schiff base type ligands with the general formula, $[o\text{-}OC_6H_4CH{=}N(CH_2)_x]_2NR^{2-}$, where $x = 3$ (saldpt) or 2 (saldien) and R = H or CH_3(me) have served to show the structural relationships involved in pentadentate complexes. With its potential to use the three N and two O ligating atoms to form four six-membered chelate rings, saldpt usually binds to five of the octahedral positions about a single metal ion [9–12]. However, saldien which forms two five and two six-membered chelate rings has been found to generate metal complexes with several different structures. Metal ions in the solid state may be bridged by saldien to form dimers in more than one way, as shown by the Cu(II) [13] and Mn(II) [5] saldien complexes. Yet, this ligand may bind to a small metal ion, such as Co(III), in an octahedral complex [14], or to a large species, such as the linear UO_2^+ [15], in a planar fashion.

There has only been a relatively small number of studies dealing with Fe complexes and more work has been done with those of Fe(II), which form Mn(saldien)-like dimers [7], than those of Fe(III). Fe(III) complexes require an additional potential ligand in order to balance the charge and this raises the question as to whether this monodentate ligand will be bound to the Fe or not. Fe(saldien)Cl and Fe(saldpt)Cl were prepared by Patton and Taylor [3]. Their infrared and electronic spectra and magnetic properties showed the complexes to be very similar, with the Cl bound to the Fe. Niswander and Martell [2] prepared, by the oxidation of the Fe(II) complex, [Fe(5-NO_2saldpt)]$_2$O·acetone and measured some of its properties. Two Fe(saldien)$^+$ units were found able to be bridged with a hydroquinone dianion [7].

The reaction of [Fe(salen)]$_2$O dissolved in DCM with nitric acid produced Fe(salen)NO_3 which was isolated from solution in two different crystalline forms [16]. One had dimeric units with monodentate bound nitrate [Fe(salen)ONO_2]$_2$ [17], while the other was monomeric with a bidentate nitrate, Fe(salen)O_2NO. When dissolved in DCM both forms produced identical solutions of Fe(salen)NO_3 which readily reacted with aqueous base to produce [Fe(salen)]$_2$O [18]. In order to gain further information about the Fe(III) pentacoordinate complexes, Fe(saldpt)NO_3 and Fe(saldien)NO_3 were prepared and then subjected to base hydrolysis. We expected to prepare the μ-oxo complexes, but they did not form. One of the products, Fe(saldpt)sal, was isolated

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**Abbreviations: PPN$^+$Cl$^-$, bis-(triphenylphosphoranylidene)ammonium chloride; DCM, dichloromethane; DMF, dimethylformamide; EtOH, ethanol; dpt, 3,3′-iminobispropylamine; medpt, 3,3′-diamino-*N*-methyldipropylamine; sal, salicylaldehyde anion; saldpt, [α,α′-[iminobis(trimethylenenitrilo)]di-*o*-cresolato(2–)]; salmedpt, [α,α′-[(methylimino-bis(trimethylenenitrilo)]di-*o*-cresolato(2–)]; saldien, [α,α′-[iminobis(dimethylenenitrilo)]di-*o*-cresolato(2–)]; salmedien, [α,α′-[(methylimino-bis(dimethylenenitrilo)]di-*o*-cresolato(2–)]; salen, *N*,*N*′-ethylenebis(salicylideneimine) dianion; 5-NO_2saldpt, 5,5′-nitro derivative of saldpt.

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in a form suitable for X-ray structural examination and it was used to identify the type of hydrolysis products obtained.

Experimental

Purification of Solvents

DCM was washed with 1 M HNO_3, 1 M NaOH and water, dried with potassium carbonate and distilled. DMF was fractionally distilled under vacuum from a mixture of 250 g DMF, 50 g benzene and 12 g of water. Vacuum was applied after the benzene, water, amines and ammonia had been distilled off. EtOH was distilled from fresh 4A zeolite.

Preparation of Compounds

The nitrates were prepared by two methods. One (Method I) was adapted from the procedure of Patton and Taylor [3] which involved the condensation of a triamine with salicylaldehyde in the presence of an Fe(III) salt and the other (Method II) involved the reaction of the base hydrolysis product (preparations described below) with nitric acid. Method II was used on a one-fifth scale to prepare the ^{15}N-labelled nitrate complexes using $H^{15}NO_3$ (Aldrich). Analyses were carried out by Galbraith Labs, Knoxville, Tenn. and Atlantic Microlab, Inc., Atlanta, Ga.

Fe(saldpt)NO$_3$

Method I. A solution containing 150 ml of EtOH, 2.02 g (20 mmol) of triethylamine and 5 ml of triethylorthoformate was prepared and warmed. 2.44 g (20 mmol) of salicylaldehyde was added in one portion with stirring, under nitrogen flow. 1.32 g (10 mmol) of dpt (Aldrich) dissolved in 15 ml of EtOH was added dropwise to the solution. The reaction mixture was stirred for 20 min. The addition funnel was washed with EtOH, then 4.04 g (10 mmol) of $Fe(NO_3)_3 \cdot 9H_2O$ dissolved in 50 ml of EtOH was added dropwise. The reaction mixture immediately changed from yellow to purple. After refluxing for 3 h, the mixture was cooled overnight and filtered. The black solid product (3.62 g) was dried at 78 °C *in vacuo* for 24 h. *Anal.* Calc. for $C_{20}H_{23}N_4O_5Fe$: C, 52.78; H, 5.09; N, 12.31; Fe, 12.27. Found: C, 52.68, 51.42, 52.16; H, 4.98, 5.42, 5.67; N, 12.17; Fe, 12.33%; N/Fe, 3.93.

Method II. Fe(saldpt)sal (0.55 g, 1.0 mmol) was dissolved in DCM (150 ml), 4 ml of freshly boiled 0.5 M HNO_3 added, and the mixture shaken for 5 min. The aqueous phase was removed, 100 ml of ether added, and the mixture allowed to stand in the refrigerator for 3 days. The solid product was obtained by filtering the solution. The product (58 mg) was dried under vacuum at 78 °C for 24 h. The IR and electronic spectra of this product were identical to those of the product prepared by Method I.

[Fe(salmedpt)]$_2$(NO$_3$)(OH)

Method I. 1.45 g (10 mmol) of medpt (Aldrich) was used as the triamine. A red–purple product (3.28 g) was obtained. *Anal.* Calc. for $C_{42}H_{51}N_7O_8Fe_2$: C, 54.45; H, 5.75; N, 10.97; Fe, 12.50. Found: C, 53.95, 53.89; H, 5.88, 5.93; N, 11.23; Fe, 12.87%; N/Fe, 3.48.

Method II. 0.47 g (1.0 mmol) of Fe(salmedpt)-OC_2H_5 was used as the starting material. The product (38 mg) had the same spectra as the product prepared by Method I.

Fe(saldien)NO$_3$

Method I. 1.03 g (10 mmol) of diethylenetriamine (Aldrich) was used. 3.40 g of the purple–black product was obtained. *Anal.* Calc. for $C_{18}H_{19}N_4O_5Fe$: C, 50.61; H, 4.48; N, 13.11; Fe, 13.07%. Found: C, 49.75; H, 4.67; N, 13.11; Fe, 12.81%; N/Fe, 4.08.

Method II. 0.48 g (1.0 mmol) $Fe(saldien)OC_2H_5 \cdot H_2O$ was used as the starting material. The product (28 mg) did not have the same IR spectrum as the product obtained by Method I. Some peaks were absent and others were broadened as if some sample decomposition had occurred.

Fe(salmedien)NO$_3$·CH$_2$Cl$_2$

Only Method I was used to prepare this nitrate. The triamine, 2,2′-diamino-*N*-methyldiethylamine, was prepared by Mann's procedure [19]. The preparation was carried out on a one-half scale using 0.550 g (4.7 mmol) of the amine. 0.64 g of a dark purple solid was obtained after recrystallization from DCM. *Anal.* Calc. for $C_{20}H_{23}N_4O_5Cl_2Fe$: C, 45.65; H, 4.41; N, 10.65; Fe, 10.61. Found: C, 45.60; H, 4.95; N, 10.88; Fe, 10.63%; N/Fe, 4.08.

The base reaction products were prepared by the reaction of the nitrate complex, dissolved in DCM, with an aqueous solution of KOH (Method I). The product was also made by condensing salicylaldehyde with the appropriate triamine in the presence of an aqueous solution of $FeSO_4$ in air (Method II).

Fe(saldpt)sal

Method I. 2.06 g (4.5 mmol) of Fe(saldpt)NO$_3$ was added to 200 ml of DCM. To this magnetically-stirred slurry was added 200 ml of 0.05 M KOH aqueous solution. After stirring for 2 h, the aqueous phase was removed and organic layer filtered. The solution was evaporated using the rotary evaporator resulting in a brown solid which was recrystallized in EtOH–H_2O (60:40, *v*/*v*). Dark purple crystals (0.72 g) were obtained after drying *in vacuo* at 78 °C for 24 h. One of these crystals was used for the X-ray examination described below. *Anal.* Calc. for $C_{27}H_{28}N_3O_4Fe$: C, 63.05; H, 5.49; N, 8.17; Fe, 10.86. Found: C, 61.05; H, 5.29; N, 8.08; Fe, 11.06%; N/Fe, 2.91.

Method II. To a magnetically-stirred solution of salicylaldehyde (2.44 g, 20 mmol) in 150 ml of EtOH–H_2O (60:40, *v/v*) was added dpt (1.32 g, 10 mmol). After stirring for 15 min at room temperature, triethylamine (2.02 g, 20 mmol) was added, and the reaction mixture was stirred for 20 min. Powdered $FeSO_4 \cdot 7H_2O$ (4.17 g, 15 mmol) in 40 ml of water was added in one portion. The reaction mixture immediately turned from homogeneous clear yellow to a dark red–purple heterogeneous mixture. This mixture was stirred at room temperature for three days. A brown solid was collected by suction filtration and washed well with water. The crude product was recrystallized three times from the EtOH–H_2O mixture. A crystalline product (82 mg) was obtained after drying *in vacuo* at 45 °C. The IR and UV-Vis spectra of this product were identical with those of the complex prepared by Method I.

Fe(salmedpt)OC₂H₅

Method I. Only a brown oil was obtained.

Method II. The same procedure was used as that for Fe(saldpt)sal except medpt was used as the triamine. A red–brown solid (58 mg) was obtained. *Anal.* Calc. for $C_{23}H_{30}N_3O_3Fe$: C, 61.07; H, 6.69; N, 9.29; Fe, 12.35. Found: C, 60.33; H, 5.90; N, 9.42; Fe, 12.64%; N/Fe, 2.97.

Fe(saldien)OC₂H₅·H₂O

Method I. 0.42 g of a brown solid was obtained. *Anal.* Calc. for $C_{20}H_{26}N_3O_4Fe$: C, 56.09; H, 6.12; N, 9.81; Fe, 13.04; molecular weight, 428.29. Found: C, 55.29; H, 5.08; N, 10.11; Fe, 13.18%; N/Fe, 3.12; molecular weight in DCM, 484.

Literature procedures were used to prepare [Fe(salen)]$_2$O [20], [Fe(5-NO_2saldpt)]$_2$O·C_3H_6O [2], and the two forms of Fe(salen)NO_3 [16].

Spectral Measurements

Electronic spectra were obtained on a Bausch and Lomb Spectronic 2000 spectrophotometer. Infrared spectra were recorded on a Nicolet Model 5DX spectrometer using samples in mineral oil and fluorocarbon mulls on a KRS-5 plate. An IBM-Bruker 200 AF spectrometer was used to record PMR spectra. Reference was set on residual solvent peaks and confirmed with external reference (TMS). Baseline corrections were made on all PMR spectra. The solutions were made at least 10 mM in the Fe complex using either DCM-d_2 or DMF-d_7 as the solvent and were examined at ambient temperature. Mössbauer spectra were measured with an Austin Science Associates, Inc., constant-acceleration spectrometer using a 1024 channel Nuclear Data ND-65 multichannel analyzer. The ^{57}Co (Rh matrix) source (New England Nuclear) had an intensity of *ca.* 40 mCi. All samples contained from 5 to 15 mg of natural iron/cm^2, sandwiched between Mylar windows and were measured at room temperature. The spectral parameters were calculated with a program labelled SHAWFIT, obtained from the Mössbauer Data Center, University of North Carolina at Asheville, Asheville, N.C. Isomer shifts are reported relative to iron foil.

Other Measurements

Magnetic moments were made using the Gouy method at room temperature with Hg[Co(SCN)]$_4$ used as the calibrant. The Evans method [21] was used to determine solution values in DCM. Conductance values were obtained with a YSI Model 32 conductance bridge with a Beckman pipet cell (cell constant = 0.001) at room temperature. Cyclic voltammetric measurements were made with a PAR Potentiostat/Galvanostat Model 273 at room temperature in DMF under nitrogen with the electroactive species at a concentration of 1 mM. Tetra-n-butyl ammonium perchlorate (TBAP) (0.1 M) was used as the supporting electrolyte. A three-electrode configuration consisting of a saturated calomel electrode, a stationary platinum working electrode and a platinum foil functioning as the auxiliary electrode was used.

Results

Preparation and Analyses

The nitrates of saldpt, saldien and salmedien were all prepared by the Patton and Taylor [3] procedure using Fe(NO_3)$_3$ instead of $FeCl_3$. However, salmedpt gave unexpectedly [Fe(salmedpt)]$_2$(NO_3)(OH). This compound was formed even when Fe(salmedpt)OC_2H_5 was reacted with nitric acid. Analysis indicated that Fe(salmedien)NO_3 retained a molecule of DCM which was the last solvent used in the preparation. The reaction of Fe(saldien)$OC_2H_5 \cdot H_2O$ with nitric acid led to some decomposition of the organic ligand as shown by the infrared spectra.

The reaction of the appropriate nitrates with aqueous base produced Fe(saldpt)sal and Fe(saldien)$OC_2H_5 \cdot H_2O$. [Fe(salmedpt)]$_2$(NO_3)(OH) gave only a brown oil. However, Fe(salmedpt)OC_2H_5 was produced when an ethanol–water solution of $FeSO_4$ was reacted in air with the ligand. This same procedure was used to produce Fe(saldpt)sal, the base hydrolysis product. Even though the samples of Fe(salmedpt)OC_2H_5, which were used for the measurements, were not made by base hydrolysis, for convenience they are labelled and discussed as if they were. The salmedien complex did not give a base hydrolysis product with a satisfactory analysis; however, the N/Fe ratio was 3.63, indicating that the product might be similar to [Fe(salmedpt)]$_2$(NO$_3$)(OH).

X-ray Crystallography

A deep purple parallelepiped crystal of Fe(saldpt)sal was glued to the end of a glass fiber, and mounted on the diffractometer. Data collection parameters are given in Table I along with crystal data. The data were corrected for Lorentz and polarization factors. An empirical absorption correction (μ(Mo Kα) = 6.54 cm^{-1}) was applied which resulted in transmission factors ranging from 0.77 to 1.00. The intensities of three representative reflections, measured periodically throughout data collection, indicated no need for a decay correction. Solution of the structure was carried out by direct methods with the SHELXS package [22]. The non-hydrogen atoms were refined anisotropically using full-matrix least-squares with the SHELXTL software. Hydrogen atoms were allowed to ride on the atom to which they were bonded, at calculated positions if bonded to carbon (C–H = 0.95 Å) or at difference Fourier positions if bonded to nitrogen, and were used for structure factor calculations, but not refined. Table II lists the atomic coordinates and equivalent isotropic thermal parameters.

TABLE I. Crystal Data for Fe(saldpt)sal

Formula	$C_{27}H_{28}N_3O_4Fe$
Formula weight	514.43
Space group	$P2_1/c$(#14)
Systematic absences	$h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$
a (Å)	12.486(5)
b (Å)	18.502(8)
c (Å)	10.870(5)
β (°)	104.23(3)
V (Å^3)	2434(2)
Z	4
D_{calc} (g/cm^3)	1.40
Crystal size (mm)	0.50 × 0.50 × 0.40
μ(Mo Kα) (cm^{-1}); correction factor range	6.54; 0.77–1.00
Data collection instrument	Nicolet R3/V
Radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)
Orientation reflections, number, range (2θ)	35, 26.4–30.0°
Temperature (°C)	21
Scan method	ω/2q
Data collection range, 2θ (°)	2–45
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	3205, 2107
No. parameters refined	317
R^a	0.047
$R_w{}^b$	0.068
Quality-of-fit indicator, S^c	0.90
Largest shift/e.s.d., final cycle	0.01
Largest peak (e/Å^3)	0.35

$^aR = \Sigma||F_{obs}| - |F_{calc}||/\Sigma|F_{obs}|$. $^bR_w = \sqrt{[(\Sigma w(|F_{obs}| - |F_{calc}|)^2/\Sigma w F_{obs}{}^2)]}$. $^cS = \sqrt{[\Sigma(|F_{obs}| - |F_{calc}|)^2/(N_o - N_v)]}$, where N_o = number of observations and N_v = number of variables.

TABLE II. Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å × 10^3)^a

	x	y	z	U_{eq}
Fe(1)	2832(1)	223(1)	1131(1)	36(1)
O(1)	1868(3)	1030(2)	1218(3)	43(1)
O(2)	3337(3)	672(2)	−300(3)	42(1)
O(3)	2525(3)	−297(2)	2564(3)	48(1)
O(4)	2637(7)	−1947(3)	4998(6)	120(3)
N(1)	1530(4)	−220(2)	−326(4)	41(2)
N(2)	3968(4)	−700(2)	1061(4)	43(2)
N(3)	4282(3)	731(3)	2253(4)	42(2)
C(1)	1196(4)	1353(3)	235(5)	44(2)
C(2)	918(5)	2086(3)	320(7)	59(2)
C(3)	233(5)	2427(4)	−700(8)	78(3)
C(4)	−218(6)	2063(4)	−1829(8)	80(3)
C(5)	−1(5)	1352(4)	−1891(6)	60(2)
C(6)	690(4)	971(3)	−880(5)	47(2)
C(7)	821(5)	201(3)	−1033(5)	47(2)
C(8)	1497(6)	−992(3)	−683(6)	59(3)
C(9)	2611(6)	−1269(3)	−783(6)	58(3)
C(10)	3425(6)	−1368(3)	476(6)	59(3)
C(11)	4707(5)	−888(3)	2301(6)	59(2)
C(12)	5497(6)	−300(4)	2925(6)	63(3)
C(13)	4948(5)	358(3)	3361(5)	53(2)
C(14)	4632(5)	1351(3)	1956(5)	46(2)
C(15)	4155(4)	1737(3)	792(5)	39(2)
C(16)	4376(6)	2475(4)	738(6)	59(3)
C(17)	3951(6)	2867(4)	−322(7)	72(3)
C(18)	3302(5)	2534(3)	−1395(6)	56(2)
C(19)	3107(5)	1800(3)	−1377(5)	49(2)
C(20)	3516(4)	1381(2)	−293(5)	40(2)
C(21)	2215(4)	−161(3)	3619(5)	41(2)
C(22)	1908(5)	532(4)	3941(6)	58(2)
C(23)	1609(6)	642(5)	5048(7)	78(3)
C(24)	1578(7)	88(5)	5891(7)	78(3)
C(25)	1884(6)	−584(5)	5608(6)	65(3)
C(26)	2202(5)	−723(3)	4493(5)	48(2)
C(27)	2541(6)	−1457(4)	4244(7)	65(3)

^{a}Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

The coordination about the Fe is approximately octahedral (Fig. 1). The saldpt ligand bonds in a pentadentate fashion similar to that observed for a binuclear μ-peroxo-cobalt(III) complex [11] and a peroxy-*p*-quinolatocobalt(III) complex [9], with the phenolic oxygen atoms in a *cis* arrangement and the three nitrogen atoms in a *mer* configuration. The sixth coordination site is occupied by the phenolic oxygen atom of the sal ligand.

The conformation assumed by the saldpt ligand appears to be largely influenced by the bulkiness of the ligand bonded to the sixth coordination site. As observed for the quinolato complex, the N–H

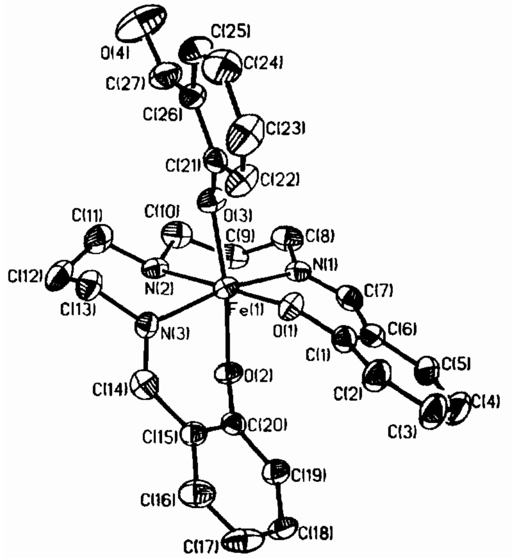

Fig. 1. Structural representation of Fe(saldpt)sal with hydrogen atoms omitted (35% probability thermal ellipsoids).

group projects toward the phenolic oxygen atom *trans* to the sixth coordination site; the salicylaldehyde groups are roughly parallel to each other and are oriented away from the sixth coordination site as well. By contrast, the conformation of the μ-peroxo has the N–H group projected toward the sixth coordination site.

The conformation adopted by the two six-membered chelate rings composed of the metal atom, an imine nitrogen atom, the central nitrogen atom and three propyl carbon atoms in Fe(saldpt)-sal is also more similar to that observed in the quinolato complex. Ring one [Fe1–N1–C8–C9–C10–N2] has a flattened chair conformation and ring two [Fe1–N2–C11–C12–C13–N3] has a more idealized chair conformation, as compared to the chair and half-chair conformations observed for the quinolato complex and chair and boat conformations observed for the μ-peroxo complex.

As observed for both the quinolato and μ-peroxo cobalt(III) complexes, the Fe1–N1 and Fe1–N3 distances (Table III) for the *trans* imine groups are essentially identical, while the bond (Fe1–N2) to the central nitrogen atom is significantly longer. The bond to the phenolic oxygen atom of the saldpt ligand (Fe1–O2), which is *trans* to the sal ligand, is longer than the other iron–phenolic oxygen distance (Fe1–O1). This lengthening of the metal–oxygen bond *trans* to the sixth coordination site was also observed in the quinolato complex.

The possibility of hydrogen bonding between the central nitrogen atom of a saldpt on one unit and the carbonyl oxygen atom of the sal ligand on another exists; however, no unusually short intermolecular contacts were observed. Without such contacts, packing interactions still play a significant role in the bonding of the sal ligand. The sal groups of

TABLE III. Selected Bond Lengths (Å) and Bond Angles (°)

Bond lengths (Å)			
Fe(1)–O(1)	1.936(4)	Fe(1)–O(2)	1.998(3)
Fe(1)–O(3)	1.947(4)	Fe(1)–N(1)	2.134(4)
Fe(1)–N(2)	2.233(4)	Fe(1)–N(3)	2.136(4)
O(1)–C(1)	1.328(6)	O(2)–C(20)	1.330(6)
O(3)–C(21)	1.322(6)	O(4)–C(27)	1.207(8)
N(1)–C(7)	1.283(7)	N(1)–C(8)	1.478(7)
N(2)–C(10)	1.477(8)	N(2)–C(11)	1.476(7)
N(3)–C(13)	1.458(7)	N(3)–C(14)	1.296(7)
C(6)–C(7)	1.448(8)	C(8)–C(9)	1.511(9)
C(9)–C(10)	1.502(9)	C(11)–C(12)	1.514(9)
C(12)–C(13)	1.528(8)	C(14)–C(15)	1.448(8)
C(26)–C(27)	1.467(9)		
Bond angles (°)			
O(2)–Fe(1)–O(1)	92.1(2)	O(3)–Fe(1)–O(1)	95.4(2)
O(3)–Fe(1)–O(2)	172.0(2)	N(1)–Fe(1)–O(1)	87.9(2)
N(1)–Fe(1)–O(2)	84.9(2)	N(1)–Fe(1)–O(3)	98.1(2)
N(2)–Fe(1)–O(1)	178.9(2)	N(2)–Fe(1)–O(2)	88.1(2)
N(2)–Fe(1)–O(3)	84.3(2)	N(2)–Fe(1)–N(1)	93.2(2)
N(3)–Fe(1)–O(1)	94.7(2)	N(3)–Fe(1)–O(2)	82.9(2)
N(3)–Fe(1)–O(3)	93.8(2)	N(3)–Fe(1)–N(1)	167.6(2)
N(3)–Fe(1)–N(2)	84.2(2)	C(1)–O(1)–Fe(1)	125.8(3)
C(20)–O(2)–Fe(1)	119.3(3)	C(21)–O(3)–Fe(1)	139.3(4)
C(7)–N(1)–Fe(1)	119.9(4)	C(8)–N(1)–Fe(1)	122.2(4)
C(8)–N(1)–C(7)	117.3(5)	C(10)–N(2)–Fe(1)	115.3(4)

(continued)

TABLE III. *(continued)*

Bond angles (°)			
C(11)–N(2)–Fe(1)	114.2(3)	C(11)–N(2)–C(10)	108.2(4)
C(13)–N(3)–Fe(1)	119.7(4)	C(14)–N(3)–Fe(1)	122.5(4)
C(14)–N(3)–C(13)	117.7(5)	C(2)–C(1)–O(1)	119.8(5)
C(6)–C(1)–O(1)	121.8(5)	C(7)–C(6)–C(1)	123.5(5)
C(7)–C(6)–C(5)	117.9(5)	C(6)–C(7)–N(1)	127.5(5)
C(9)–C(8)–N(1)	112.3(5)	C(10)–C(9)–C(8)	113.9(5)
C(9)–C(10)–N(2)	115.2(5)	C(12)–C(11)–N(2)	115.6(5)
C(13)–C(12)–C(11)	114.8(5)	C(12)–C(13)–N(3)	109.2(5)
C(15)–C(14)–N(3)	124.2(5)	C(16)–C(15)–C(14)	118.4(5)
C(20)–C(15)–C(14)	121.8(5)	C(15)–C(20)–O(2)	121.6(5)
C(19)–C(20)–O(2)	121.1(5)	C(27)–C(26)–C(21)	120.5(6)
C(26)–C(21)–O(3)	119.9(5)	C(22)–C(21)–O(3)	123.0(5)
C(27)–C(26)–C(25)	119.3(6)	C(26)–C(27)–O(4)	123.7(7)

molecules related by an inversion center at ($x = 0.0$, $y = 0.0$, $z = 0.5$), lie in an overlapping fashion with their planes parallel, with an average distance between the planes of 3.94 Å. This intermolecular packing arrangement forces the sal group to be oriented nearly along the Fe1–O1 bond, resulting in a great deal of intramolecular steric repulsion as is evidenced by the bond angles (Table III): O1–Fe1–O3, N2–Fe1–O3, Fe1–O3–C21 and O3–C21–C22.

Electronic Spectra

The electronic spectra of the iron nitrates were obtained at 0.1 mM in DMF, DCM and DMF containing 0.2 mM NaOH, while spectra of the base hydrolysis products were obtained in DMF and DCM. Table IV gives the major spectral bands and the log ϵ values. The majority of the spectra had an intense visible band at about 500 nm which is considered to be a ligand-to-metal charge transfer band for these types of Fe(III) complexes [23]. The order of increasing energy for this band is: salen < saldien < salmedien < salmedpt < saldpt. All of the complexes had an intense near ultraviolet band around 320 nm and most showed an intense shoulder in the range 419 to 436 nm. Fe(saldpt)NO_3 and [Fe(saldpt)]$_2$(NO_3)(OH) exhibited little difference between each spectrum in DCM and those in DMF; however, the saldien, salmedien, and salen complexes had different spectra in the two solvents. The presence of two equivalents of OH^- in the DMF solutions of the nitrates resulted in spectra which for the saldpt, salmedpt and saldien complexes were the same in DMF as that for the base hydrolysis products in DMF. The base hydrolysis products of saldpt, salmedpt and saldien each had essentially the same spectrum in both DMF and DCM.

PMR Spectra

The PMR spectral bands for the Fe(III) complexes are given in Table IV and the spectra for Fe(saldpt)NO_3 and Fe(salmedpt)OC_2H_5 in DMF-d_7 and [Fe(salmedpt)]$_2$(NO_3)(OH) in DCM-d_2 are shown in Fig. 2. Because of low solubility the nitrates, except for [Fe(salmedpt)]$_2$(NO_3)(OH), were examined in DMF-d_7. All of the compounds had spectra with peaks lying within a 160 ppm range which is expected

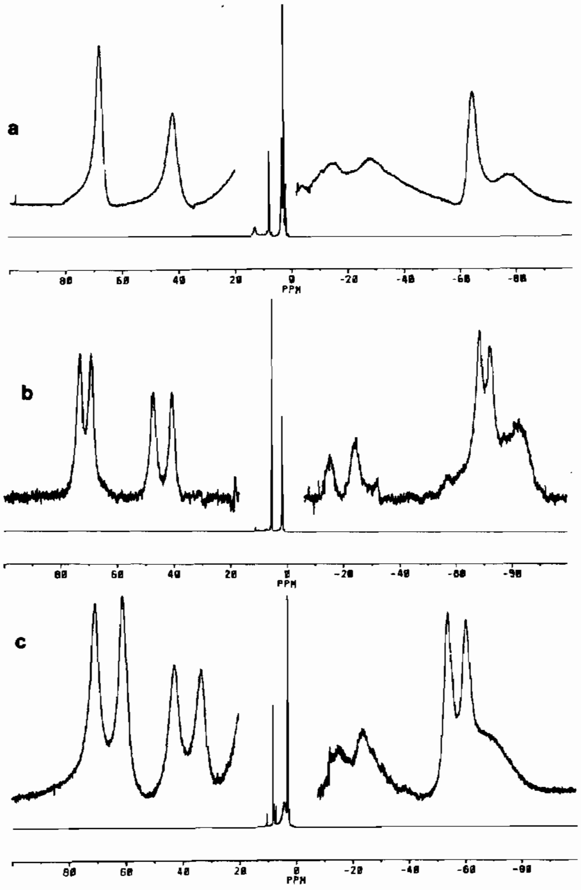

Fig. 2. PMR spectra of: (a) Fe(saldpt)NO_3 in DMF-d_7; (b) [Fe(salmedpt)]$_2$(NO_3)(OH) in DCM-d_2; (c) Fe(salmedpt)-OC_2H_5in DMF-d_7.

TABLE IV. Solution Data for the Fe(III) Complexes

Compound[a]	Spectral bands						Conductivity[d] (ohm^{-1} cm^2 mol^{-1})	Cyclic voltammetry (V)[e]	
	Electronic (nm)[b]	PMR (ppm)[c]						$E_{p,a}$	$E_{p,c}$
		3-H	4-H	5-H	6-H	non-ring			
Fe(saldpt)NO_3	C 506(3.27), 326(3.90)	D + 78.0	−67.7	+64.9	−41.8	+28	C 4.8	−0.132	−0.360
	D 502(3.34), 322(3.91)					+15	D 73.1	−0.51	−0.94
	H 471sh(3.5), 426sh(3.5), 320(4.04)							−0.85	−1.168
[Fe(salmedpt)]$_2$(NO_3)(OH)	C 526(3.30), 438sh(3.3), 326sh(4.0)	C + 82.9	−72.9	+72.8	−47.0	+25	C 5.1	−0.092	−0.312
	D 516(3.20), 436sh(3.3), 321(3.90)		−69.1	+68.1	−40.3	+16	D 75.2	−0.52	−0.858
	H 480sh(3.5), 432sh(3.5), 323(4.04)	D + 69	−69.1	+61.0	−43.0	+24		−0.825	−1.104
			−60.8	+54.2	−33.5	+17			
Fe(saldien)NO_3	C 515(3.48), 434sh(3.3), 322(4.00)	D + 85	−83.1	+75.3	−47.9		C 7.1	−0.353	−0.452
	D 503(3.70), 431sh(3.5), 319(4.00)						D 62.9		−0.58
	H 460sh(3.6), 420(3.60), 316(4.04)								
Fe(salmedien)$NO_3 \cdot CH_2Cl_2$	C 517(3.90), 324(4.36)	D + 84	−85.0	+76.5	−49.4		C 11.5	−0.335	−0.431
	D 509(3.60), 432(3.30), 322(3.95)		−78.0		−43.6		D 68.2		−0.67
	H 462sh(3.6), 419sh(3.7), 316sh(4.0)								
Fe(salen)NO_3	C 532(4.11), 322(4.46)	D + 80.2	−70.6	+57.7	−40.9		C 0	−0.234	−0.375
	D 480(3.48), 316(4.04)	C + 97	−82	+81	−53		D 63.9		−1.01
	H 460sh(3.3)								
Fe(saldpt)sal	C 469sh(3.3), 426sh(3.3), 322(3.95)						C 0.8	−0.238	−0.482
	D 469sh(3.3), 425sh(3.3), 321(3.85)						D 9.0	−0.60	−0.818
									−0.98
									−1.20
Fe(salmedpt)OC_2H_5	C 482sh(3.5), 433sh(3.5), 323(3.90)	C + 72	−70.7	+60.8	−42.5		C 0.5	−0.154	−0.310
	D 478sh(3.3), 433sh(3.3), 327(3.85)		−58.7	+51.2	−34.2		D 7.1	−0.65	−0.75
		D + 69	−70.7	+60.7	−42.7	+24		−1.11	
			−60.9	+53.9	−33.1	+16			
Fe(saldien)OHC_2H_5OH	C 462sh(3.7), 414(3.78), 318(4.20)						C 14.8	−0.472	−0.575
	D 460sh(3.7), 416(3.78), 314(4.15)						D 27.1	−0.792	−0.842

[a] See text for abbreviations. [b] Solvent symbols: C, DCM; D, DMF; H, DMF with two moles of NaOH present per mole of iron, log ϵ values in parentheses. Iron concentration at 0.1 mM. [c] Iron concentration at least 1 mM. [d] Iron concentration at 1 mM. The Λ_m values for PPN^+Cl^-, a 1:1 electrolyte, are 67.4 (DCM) and 59.7 (DMF) ohm^{-1} cm^2 mol^{-1}. [e] Iron concentration at 1 mM.

for high spin Fe(III) Schiff base complexes [24]. The nitrate complexes of saldpt and saldien had spectra like that of Fe(salen)NO_3 with an alternating chemical shift pattern for the phenyl resonances [16]. Assignments were made based on the values for this nitrate. The band due to the 3-H phenyl proton was in some cases broad and not as well defined as that for the often overlapping 5-H band. The spectra of the saldpt and salmedpt complexes showed broad bands at about +24 and +16 ppm which were assumed to be due to the non-ring protons. The spectra of [Fe(salmedpt)$]_2$(NO_3)(OH) in DCM-d_2 and DMF-d_7 and Fe(salmedpt)OC_2H_5 in DMF-d_7 showed a doubling effect with two peaks present for each of the phenyl resonances. The spectra of [Fe(salmedpt)$]_2$(NO_3)(OH) in DCM-d_2 and Fe(salmedpt)OC_2H_5 in DMF-d_7 were nearly identical. The separations between peak pairs in the [Fe(salmedpt)$]_2$(NO_3)(OH) spectrum in DCM-d_2 were smaller than those found for the DMF-d_7 spectrum. The Fe(salmedpt)OC_2H_5 DCM-d_2 spectrum showed bands at positions similar to those found in the DMF-d_7 spectrum. However, there were extra bands at −55.7, −28.2 and +47.1 ppm in the DCM spectrum. These probably arise at least, in part, from the OC_2H_5 groups. Fe(saldpt)sal and Fe(saldien)$OC_2H_5 \cdot H_2O$ had DCM-d_2 spectra with a very large number of resonances.

The doubling effect has been examined in some detail and has occurred when paramagnetic complexes, such as Ni(saldpt) and Ni(salmedpt), were dissolved in a non-coordinating solvent [1]. The doubling for the Ni complexes was found to be due to the presence of only one species in solution and a pentadentate ligand coordination which results in the two salicylaldimine fragments being non-equivalent in some major respect. The two aromatic fragments were assumed to be oriented differently with respect to the major axes of the chelate. The phenyl non-equivalence for the Ni(II) complexes appeared to arise from the actual structure lying somewhere between a trigonal bipyramid and a square pyramid structure. For the Fe complexes the doubling is found in the salmedpt complexes, and to a smaller degree, in the salmedien ones, not with the saldpt or saldien complexes. Apparently, the introduction of a methyl group into the saldpt and saldien ligands produces significant asymmetry in the complex.

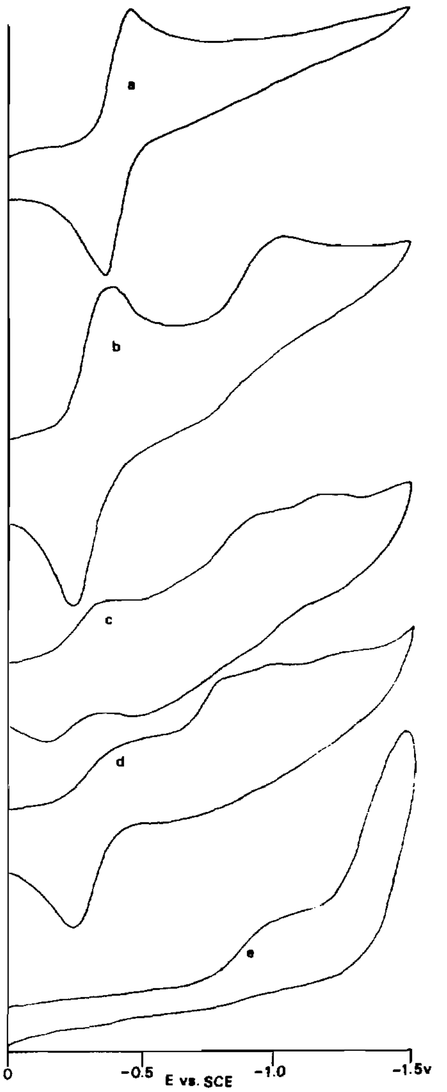

Fig. 3. Cyclic voltammograms of: (a) Fe(saldien)NO_3; (b) Fe(salen)NO_3; (c) Fe(saldpt)NO_3; (d) Fe(saldpt)sal; and (e) [Fe(5-NO_2saldpt)$]_2O \cdot C_3H_6O$ in DMF solution at room temperature (scan speed 100 mV s^{-1}; reference electrode SCE).

Cyclic Voltammetry

The electrochemistry of the Fe(III) complexes was investigated in dry DMF under nitrogen with 0.1 M TBAP as the supporting electrolyte. The cyclic voltammograms of Fe(saldpt)NO_3, Fe(saldpt)sal, Fe(saldien)NO_3, Fe(salen)NO_3 and [Fe(5-NO_2-saldpt)$]_2O \cdot C_3H_6O$ are shown in Fig. 3 and the data for all of the complexes, except the latter, are given in Table IV. Measurements were made with an initial potential of 0.00 V and a switching potential of −1.5 V since the five coordinate complexes were electroactive in this range, but not in the 0 to +1.0 V range. All of the complexes showed only irreversible electroreduction processes under the conditions employed.

The first electroreduction process for the nitrates had $E_{p,c}$ and $E_{p,a}$ values from about −0.1 to −0.5 V. Complexes of similar nature have 3+/2+ Fe reduction in this range [25]. The order of the potentials for the first process of the nitrates is: saldpt > salen = salmedien ~ saldien.

TABLE V. Solid State Data for Fe(III) Complexes

Compound	Important IR bands (cm^{-1})[a]	Mössbauer Spectra Parameters (mm s^{-1})[b]		Magnetic moment (BM)[b,c]
		δFe	Δ	
Fe(saldpt)NO$_3$	N 1380(?), 1035, 826 NH 3370	0.54	0.75(LN)	5.6
[Fe(salmedpt)]$_2$(NO$_3$)(OH)	N 1380(?), 1037 OH 3411	0.39	0.85(RT)	5.3
Fe(saldien)NO$_3$	N 1480, 1267, 1005 NH 3300	0.41	0.75(RT)	5.5
Fe(salmedien)NO$_3$	N 1482, 1283, 1028	0.60	0.45(LN)	5.5
[Fe(salen)ONO$_2$]$_2$	N 1486, 1283, 1033	0.40 0.51	1.56(RT) 1.55(LN)	5.5
Fe(saldpt)sal	NH none	0.37	0.74(RT)	5.8 6.0sn
Fe(salmedpt)OC$_2$H$_5$	OH 3370	0.36	0.95(RT)	5.0 5.1sn
Fe(saldien)OC$_2$H$_5$·H$_2$O	NH & OH 3400 br	0.53	0.88(LN)	5.1 4.9sn
[Fe(salen)]$_2$O	O 825[d]	0.32 0.41	0.72(RT)[e] 0.46(LN)	1.94[e]
[Fe(5-NO$_2$saldpt)]$_2$O·C$_3$H$_6$O	O 810[f]	0.42	1.25(RT)	1.89[f]

[a] From mull spectra; important bands: N, nitrate; NH, amine H; OH, hydroxy; O, μ-oxo. [b] Room temperature (RT) and liquid nitrogen (LN) values. [c] Solid measurements; sn, DCM solution measurements. [d] Ref. 20. [e] Ref. 26. [f] Ref. 2.

Fe(saldien)NO$_3$ and Fe(saldpt)sal have different CVs; while [Fe(salmedpt)]$_2$(NO$_3$)(OH) and Fe(salmedpt)OC$_2$H$_5$ have nearly identical ones. The CV of Fe(saldien)NO$_3$ resembles that of Fe(salen)NO$_3$, but is different from that of Fe(saldien)OC$_2$H$_5$·H$_2$O.

The effect of changing the Schiff base structure and nature of the Fe(III) complexes on the electrochemistry is shown in Fig. 3. Fe(saldien)NO$_3$ and Fe(saldpt)NO$_3$ have similar CVs, while that of Fe(saldpt)NO$_3$ and Fe(saldpt)sal are much different. The CV of [Fe(5-NO$_2$saldpt)]$_2$O·C$_3$H$_6$O is remarkably unlike the others.

Infrared Spectra

The important infrared bands of the complexes are shown in Table V. Fe(saldien)NO$_3$ and Fe(salmedien)NO$_3$ had nitrate bands at approximately the same wave numbers as those for [Fe(salen)ONO$_2$]$_2$ which has monodentate bound nitrate [16]. The bands were identified by preparing the ^{15}N labelled nitrate complexes and comparing labelled and unlabelled spectra. The saldpt and salmedpt nitrate complexes also had bands indicative of bound nitrate, but they were not as well defined since there were many more bands due to the organic ligand, preventing a definite assignment. The 1380 cm^{-1} region of both complexes seemed to be shifted in intensity upon comparing spectra. The only band which clearly shifted was the one at ~1035 cm^{-1} which is a band not expected for ionic nitrate [27]. Fe(saldien)NO$_3$ and Fe(saldpt)NO$_3$ showed what was assumed to be a weak band due to N–H at ~3300 cm^{-1}; yet the base hydrolysis products did not show this band. This band is known to be weak and sometimes has not been observed [3].

Mössbauer Spectra

The spectra of the Fe(III) complexes were recorded at liquid nitrogen or room temperature and the parameters, for all except the salen and 5-NO$_2$-saldpt μ-oxo complexes, are indicative of high spin Fe(III) complexes. The nitrates with pentadentate ligands had smaller Δ values than that of [Fe(salen)ONO$_2$]$_2$ [16]. The spectra for the nitrates and base hydrolysis products were quite similar with about the same parameters and unsymmetrical peaks. The μ-oxo spectra, on the other hand, had sharper, more symmetrical peaks. It is interesting to note the large Δ for [Fe(5-NO$_2$saldpt)]$_2$O compared to the values for the other pentacoordinate complexes.

Magnetic Properties

All of the nitrates displayed slightly depressed magnetic moments at room temperature. For [Fe(salen)ONO$_2$]$_2$ this is due to a small amount of antiferromagnetic coupling of the iron atoms in the dimer which exists only in the solid state [16]. The monomer, Fe(salen)O_2NO, has the expected moment (5.9 BM) for a high-spin Fe(III) complex at room temperature. Both forms in solution gave the same monomeric species, showing no antiferromagnetic nature. The low moment of the pentadentate nitrates is difficult to explain and warrants more extensive examination of their magnetic properties.

The three base hydrolysis products were examined both in DCM solution and in the solid state. Fe(saldpt)sal had a normal moment; while the salmedpt and saldien products had low moments. There was no significant difference between the solid and solution values.

Discussion

The saldpt nitrate complex in the solid state is a high-spin Fe(III) complex with a weakly bound nitrate, while those of saldien and salmedien have a similar nature, but with a strongly bound, monodentate nitrate. The saldpt complex had about the same electronic spectrum in both DCM and DMF; however, the saldien and salmedien complexes showed a definite difference, as found with Fe(salen)NO_3. In DMF all of the nitrate complexes had conductance values close to that expected for a 1:1 electrolyte. The complexes in DCM showed a small amount of conductivity. In DCM, Fe(saldpt)NO_3 must exhibit weak association with the nitrate ion and/or other $Fe(saldpt)^+$ units. The latter association might account for the low magnetic moments found in the solution and solid states. The saldien ligand is known to bridge metal ions [5, 13] and this type of association may take place, providing a mechanism for the antiferromagnetic interaction.

Some base hydrolysis of the saldpt ligand must occur to produce sal, used to form Fe(saldpt)sal. Acid hydrolysis of the Schiff bases is well-known [28], but base hydrolysis was unexpected. The electronic spectra of a basic DMF solution of Fe(saldpt)NO_3 is essentially that of Fe(saldpt)sal in DMF even though the latter complex does not ionize appreciably. In fact, Fe(saldpt)sal does not ionize much in either DCM or DMF and it has a magnetic moment expected for a high-spin Fe(III) complex. This complex appears to maintain its structural integrity in both the solid and solution states.

The base hydrolysis product of Fe(saldien)NO_3 is shown as Fe(saldien)$OC_2H_5 \cdot H_2O$, corresponding to the product Fe(salmedpt)OC_2H_5. The two compounds have nearly identical spectra. The saldien product may also be written as Fe(saldien)OH$\cdot C_2H_5OH$. A μ-oxo formulation is not considered since the compound has no properties of that nature. At this time there is no unequivocal way to determine the exact formula of the saldien compound.

A most unusual complex was that of [Fe(salmedpt)]$_2$(NO_3)(OH) which was the product of the Patton and Taylor [3] preparation method, as well as the reaction of nitric acid with Fe(salmedpt)OC_2H_5. Many of the compound's solid and solution properties were similar to those for Fe(saldpt)NO_3. The two solids had essentially the same Mössbauer spectra and nearly equal magnetic moments at room temperature. The cyclic voltammograms of the two in DMF were alike and the addition of base to both DMF solutions produced significant spectral changes. A primary difference between the two was that the salmedpt compound was soluble enough in DCM for a PMR spectrum to be measured; while this was not possible for the saldpt complex. [Fe(salmedpt)]$_2$(NO_3)(OH) showed a clear example of double peaks in its PMR spectrum in DCM. Further study will be required in order to determine if the salmedpt complex has an OH bridge between the two irons and an ionic nitrate.

Supplementary Material

Full tables of bond distances and angles and calculated structure factors for Fe(saldpt)sal may be obtained from the author W.T.P.

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