A Family of High-Spin $FeS_2N_2O_2$ Complexes Incorporating Fe^{III}–S(thioether) Binding

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Introduction

This work stems from our interest in the chemistry of complexes incorporating metal–thioether binding.[1-4] The results reported here concern trivalent iron. During the last two decades or so iron–sulfur chemistry based on sulfide and thiolate ligands has witnessed remarkable progress.[5] Thioether complexes of iron have also received significant attention, but mostly in the case of the bivalent metal.[6-8] Few authentic Fe^{III}–S (thioether) species have been isolated and characterized in a pure state.[9-11] The hardness of iron(III) has been cited as a possible reason for this.[6a] Herein we report a family of stable high-spin complexes of coordination type $Fe^{III}S_2N_2O_2$ derived from hexadentate triazene 1-oxide thioether ligands. The presence of Fe^{III}–S(thioether) binding has been authenticated by structure determination in one case. Spectra, magnetism, and redox properties are described.

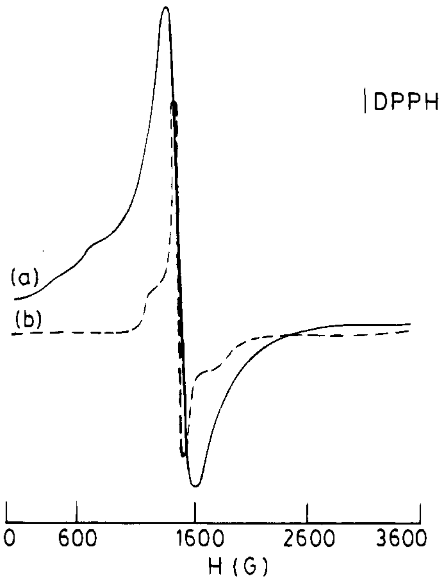
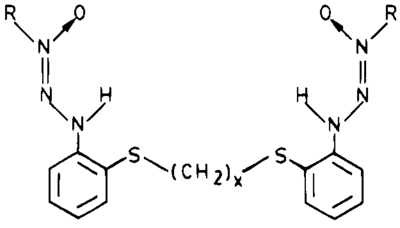


Figure 1. EPR spectra at X-band of $[Fe(Me3L)]ClO_4$ in the polycrystalline state at 77 K (—, a); of $[Fe(Me2L)]ClO_4$ in acetonitrile–toluene (1:1) at 77 K (- -, b). Instrument settings: power, 30 dB; modulation, 100 kHz; sweep center, 3000 G; sweep width, 8000 G; sweep time, 240 s; microwave frequency, 9.10 GHz.

Results and Discussion

Synthesis and Characterization. Our familiarity[2-4] with the hexadentate ligands of type **1** (H_2RxL) led us to try them as possible chelators of trivalent iron. The reaction of H_2RxL with



H_2RxL

R = Me, Ph ; x = 2,3

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iron(III) nitrate nonahydrate in dichloromethane–methanol followed by addition of sodium perchlorate afforded complexes of composition $[Fe(RxL)]ClO_4$ in excellent yields.

Selected characterization data are given in Table 1. The complexes are high-spin ($t_2{}^3e^2$) and their EPR spectra (Figure 1) are characterized by a predominant feature near $g = 4$, suggesting rhombic symmetry[12] for the spin-free d^5 ion. This is in agreement with the severely distorted geometry revealed in the X-ray structure of $[Fe(Me3L)]ClO_4$.

Structure. The lattice of $[Fe(Me3L)]ClO_4$ consists of discrete cations (Figure 2) and anions. Selected bond parameters for $[Fe(Me3L)]^+$ are collected in Table 2. Both of the thioether

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Table 1. Characterization Data

compd	UV−vis data;[a] λ_{max}, nm (ϵ, M^{-1} cm^{-1})	$E_{1/2}$,[a−c] V (ΔE_p, mV[d])	n[e,f]	μ_{eff},[g] μ_B	EPR g values
[Fe(Me2L)]ClO$_4$	680 (1660), 470[h] (840)	0.16 (70)	0.96	5.81	4.13,[i] 4.21[j]
[Fe(Ph2L)]ClO$_4$	750 (2160), 540 (1447)	0.23 (80)	0.98	5.75	4.14,[i] 4.19[j]
[Fe(Me3L)]ClO$_4$	650 (2170), 460[h] (824)	0.02 (130)	0.94	5.79	4.15,[i] 4.87;[h,j] 4.22,[j] 3.57[h,j]

[a] Solvent is acetonitrile. [b] At a platinum electrode; the supporting electrolyte is tetraethylammonium perchlorate (TEAP, 0.1 M); scan rate, 50 mV s^{-1}; reference electrode, SCE; solute concentration, $\sim 10^{-3}$ M. [c] $E_{1/2}$ is calculated as the average of anodic (E_{pa}) and cathodic (E_{pc}) peak potentials. [d] $\Delta E_p = E_{pa} - E_{pc}$. [e] Constant-potential coulometric data $n = Q/Q'$, where Q is the observed coulomb count and Q' is the calculated count for 1e transfer. [f] Electrolysis performed at 200 mV above E_{pa} for oxidation. [g] In the solid state at 298 K. [h] Shoulder. [i] Polycrystalline state at 77 K. [j] Dichloromethane−toluene (1:1) at 77 K.

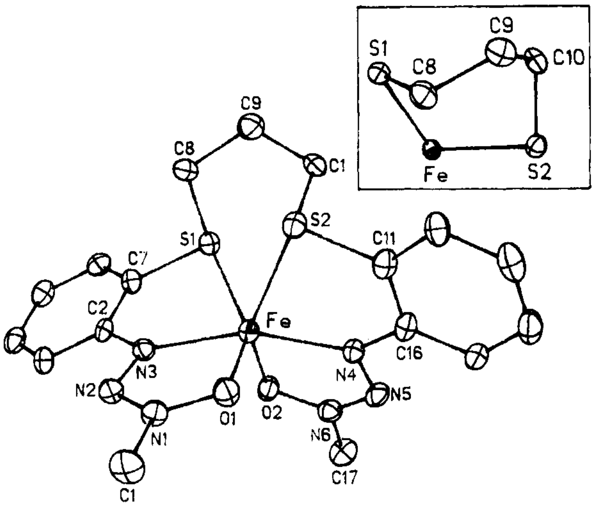

Figure 2. ORTEP plot and labeling scheme for [Fe(Me3L)]$^+$ in [Fe(Me3L)]ClO$_4$ with all atoms represented by their 50% probability ellipsoids.

Table 2. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for [Fe(Me3L)]ClO$_4$

	Distances		
Fe−S(1)	2.557(2)	O(1)−N(1)	1.330(8)
Fe−S(2)	2.533(2)	O(2)−N(6)	1.318(8)
Fe−O(1)	2.013(5)	N(1)−N(2)	1.267(9)
Fe−O(2)	2.011(5)	N(2)−N(3)	1.319(9)
Fe−N(3)	2.016(6)	N(4)−N(5)	1.329(9)
Fe−N(4)	2.020(6)	N(5)−N(6)	1.279(9)
	Angles		
O(1)−Fe−O(2)	112.8(2)	O(2)−Fe−S(2)	145.7(2)
O(1)−Fe−N(3)	75.0(2)	N(3)−Fe−N(4)	159.5(2)
O(1)−Fe−N(4)	93.2(2)	N(3)−Fe−S(1)	78.1(2)
O(1)−Fe−S(1)	147.9(2)	N(3)−Fe−S(2)	117.3(2)
O(1)−Fe−S(2)	89.4(2)	N(4)−Fe−S(1)	117.4(2)
O(2)−Fe−N(3)	94.3(2)	N(4)−Fe−S(2)	78.5(2)
O(2)−Fe−N(4)	74.7(2)	S(1)−Fe−S(2)	87.7(1)
O(2)−Fe−S(1)	86.1(2)		

functions are coordinated. The FeS$_2$N$_2$O$_2$ coordination sphere is severely distorted from an octahedral symmetry. The cis and trans coordination angles around the iron atom lie in the ranges 75.0(2)−117.4(2)° and 145.7(2)−159.5(2)°, respectively. The five-membered rings incorporating N,O and N,S chelation are planar. The six-membered FeS$_2$C$_3$ ring has a skew-boat configuration (inset, Figure 2).

The two Fe^{III}−S(thioether) lengths are 2.557(2) and 2.533(2) Å. Only three complexes with Fe^{III}−S(thioether) binding have been structurally characterized as all low-spin.[9,10] The Fe^{III}−S(thioether) lengths in them lie in the range of 2.28−2.38 Å. The average length in our high-spin complex is ~0.2 Å longer. To our knowledge [Fe(Me3L)]ClO$_4$ represents the first example of a structurally characterized high-spin trivalent iron ligated with thioether functions.

Reduction. The complexes display a quasireversible iron(III)−iron(II) couple having $E_{1/2}$ in the range 0.02−0.23 V vs SCE (Table 1). The red iron(II) complex Fe(R*x*L) can be isolated by the reduction of the trivalent precursor with hydrazine hydrate. They are high-spin ($t_2^4e^2$) with μ_{eff} in the range 4.93−5.08 μ_B. In solution they are quantitatively reoxidized to Fe(R*x*L)$^+$ by hydrogen peroxide. The cyclic voltammogram of Fe(R*x*L) (initial scan anodic) is the same as that of Fe(R*x*L)$^+$ (initial scan cathodic).

Concluding Remarks

It is demonstrated that the H$_2$R*x*L ligands afford complexes of type [Fe(R*x*L)]ClO$_4$ which are high-spin and display iron(III)−iron(II) reduction at relatively low potentials. The salt [Fe(Me3L)]ClO$_4$ represents the first structurally characterized high-spin iron(III) complex incorporating thioether binding. The paucity of such species is probably due to lack of planned search rather than inherent instability.

Experimental Section

Materials. The purification of acetonitrile and dichloromethane and the preparation of tetraethylammonium perchlorate (TEAP) for electrochemical work were done as before.[13] All other chemicals and solvents were of analytical grade and were used as received. The ligands H$_2$R*x*L were prepared following reported methods.[2d,4e,14,15]

Physical Measurements. Electronic spectra were recorded with a Hitachi 330 spectrophotometer. Magnetic susceptibilities of solids were measured by using a PAR-155 vibrating sample magnetometer fitted with a Walker Scientific L75FBAL magnet, and EPR spectra were recorded in the X-band using a Varian 109C spectrometer fitted with a quartz dewar. Calibration was done with DPPH (g = 2.0037). A Perkin-Elmer 240C elemental analyzer was used to collect microanalytical data (C, H, N). Electrochemical measurements were performed on a PAR Model 370-4 electrochemistry system as reported earlier.[13] All potentials in this work are incorrected for junction contribution. Solution ($\sim 10^{-3}$ M) electrical conductivities were measured with the help of a Philips PR 9500 bridge.

Preparation of Complexes. [1,2-Bis((*o*-(1-phenyl-1-oxidotriazen-3-yl)phenyl)thio)ethanato-*N*^{3},*S*,*O*]iron(III) Perchlorate, [Fe(Ph2L)]ClO$_4$. [*Caution*! ***Perchlorate salts of metal complexes with organic ligands are explosive.***] A methanolic solution (15 mL) of KOH (0.087 g, 1.55 mmol) was added to a dichloromethane solution (20 mL) of 0.40 g (0.77 mmol) of the ligand H$_2$Ph2L and the solution was stirred in air at room temperature for 0.5 h. A methanolic solution (15 mL) of Fe(NO$_3$)$_3$·9H$_2$O (0.313 g, 0.77 mmol) was then added. After a few minutes of stirring, solid NaClO$_4$·H$_2$O (0.109 g, 0.77 mmol) was added to the reaction mixture which was then stirred for another hour. A green precipitate was collected by filtration and washed with water and methanol. The product was finally dried in vacuo. The yield was 0.36 g (~70%). Anal. Calcd for $C_{26}H_{22}N_6O_6S_2ClFe$: C, 46.60; H, 3.28; N, 12.54. Found: C, 46.47; H, 3.23; N, 12.31.

The blue complexes [Fe(Me2L)]ClO$_4$ and [Fe(Me3L)]ClO$_4$ were prepared similarly (yield ~72%). Anal. Calcd for $C_{16}H_{18}N_6O_6S_2ClFe$ ([Fe(Me2L)]ClO$_4$): C, 35.19; H, 3.30; N, 15.40. Found: C, 35.17; H,

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Table 3. Crystallographic Data for [Fe(Me3L)]ClO_4

chem formula	$C_{17}H_{20}N_6O_6S_2ClFe$	T, °C	23
fw	559.8	λ, Å	0.71073
space group	$P2_1/n$	ϱ_{calcd}, g cm^{-3}	1.643
a, Å	8.965(3)	μ, cm^{-1}	10.20
b, Å	17.912(6)	transm coeff	0.7379−0.7568
c, Å	14.262(4)	R,[a] %	4.50
β, deg	98.84(3)	R_w,[b] %	4.53
V, Å^3	2263(1)	GOF[c]	0.55
Z	4		

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2(|F_o|) + g|F_o|^2$; $g = 0.0001$. [c] The goodness of fit is defined as $[w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$, where n_o and n_v denote the numbers of data and variables, respectively.

2.91; N, 15.48. Anal. Calcd for $C_{17}H_{20}N_6O_6S_2ClFe$ ([Fe(Me3L)]ClO_4): C, 34.22; H, 3.21; N, 14.97. Found: C, 34.02; H, 3.31; N, 14.80. The complexes are 1:1 electrolytes in acetonitrile solution (Λ = 110−115 Ω^{-1} cm^2 M^{-1}).

Reduction. To a 20 mL dichloromethane solution of [Fe(Ph2L)]ClO_4 (0.200 g, 0.29 mmol) was added 10 mL of methanol and the mixture was stirred at room temperature. To it was added 0.5 mL of hydrazine hydrate. After 0.5 h of further stirring the red precipitate was collected by filtration and washed with water and methanol. The product was dried in vacuo. The yield was 0.145 g (~85%). Anal. Calcd for $C_{26}H_{22}N_6O_2S_2Fe$: C, 54.78; H, 3.86; N, 14.75. Found: C, 54.67; H, 3.77; N, 14.86.

The complexes Fe(Me2L) and Fe(Me3L) were prepared following the same procedure (yield ~85%). Anal. Calcd for $C_{16}H_{18}N_6O_2S_2Fe$ (Fe(Me2L)): C, 43.10; H, 4.06; N, 18.85. Found: C, 43.40; H, 3.86; N, 18.74. Anal. Calcd for $C_{17}H_{20}N_6O_2S_2Fe$ (Fe(Me3L)): C, 44.40; H, 4.35; N, 18.28. Found: C, 44.15; H, 4.39; N, 18.51.

X-ray Structure Determination. Cell parameters of [Fe(Me3L)]ClO_4 (0.12 × 0.13 × 0.32 mm^3) grown by slow diffusion of n-hexane into dichloromethane solution were determined by least-squares fits of 30 machine-centered reflections (2θ = 15−30°). Systematic absences led to unequivocal space group identification as $P2_1/n$. Data were collected by the ω-scan method (2θ = 2−50°) on a Nicolet R3m/V diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. Two check reflections measured after every 98 reflections showed no significant intensity reduction during ~38-h exposure to X-rays. Data were collected for Lorentz−polarization effects and absorption.[16] Of the 4438 reflections collected, 4008 were unique of which 1758 satisfying $I > 3\sigma(I)$ were used for structure solution.

The structure was solved by direct methods. All non-hydrogen atoms were made anisotropic. Hydrogen atoms were added at calculated positions with fixed U = 0.08 Å^2. All refinements were done by full-matrix least-squares procedures. The highest residual was 0.44 e/Å^3. All calculations were done on MicroVax II computer with the programs of SHELXTL-PLUS.[17] Significant crystal data are listed in Table 3. Atomic coordinates and isotropic thermal parameters are presented in Table 4.

Table 4. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for [Fe(Me3L)]ClO_4[a]

	x	y	z	U(eq)
Fe	2062(1)	9794(1)	1974(1)	32(1)
Cl	1937(3)	2155(1)	4973(2)	61(1)
S(1)	368(2)	9054(1)	2926(1)	34(1)
S(2)	4303(2)	9169(1)	2965(1)	35(1)
O(1)	3215(5)	9824(3)	870(3)	42(2)
O(2)	510(6)	10610(3)	1923(4)	41(2)
O(3)	3311(11)	1862(6)	5331(9)	146(5)
O(4)	844(12)	1627(6)	4642(7)	137(5)
O(5)	1469(12)	2550(6)	5752(7)	121(4)
O(6)	2041(9)	2664(4)	4233(5)	88(3)
N(1)	2532(7)	9466(3)	106(5)	36(2)
N(2)	1295(7)	9128(3)	123(4)	34(2)
N(3)	832(6)	9175(3)	956(4)	31(2)
N(4)	3175(7)	10681(3)	2616(4)	34(2)
N(5)	2467(8)	11334(3)	2593(5)	38(2)
N(6)	1080(8)	11259(4)	2230(5)	39(2)
C(1)	3234(10)	9481(5)	−744(6)	54(3)
C(2)	−571(8)	8854(4)	1011(5)	28(2)
C(3)	−1602(8)	8651(4)	234(6)	36(3)
C(4)	−2997(9)	8368(4)	358(6)	44(3)
C(5)	−3363(9)	8280(4)	1257(6)	42(3)
C(6)	−2343(9)	8480(4)	2039(6)	40(3)
C(7)	−945(8)	8773(4)	1921(5)	33(3)
C(8)	1479(9)	8209(4)	3183(5)	39(3)
C(9)	2653(10)	8339(5)	4057(6)	46(3)
C(10)	3577(9)	9043(4)	4074(5)	38(3)
C(11)	5383(8)	10002(4)	3202(5)	37(3)
C(12)	6923(8)	9948(5)	3580(6)	43(3)
C(13)	7745(10)	10592(6)	3741(6)	55(4)
C(14)	7081(10)	11282(5)	3548(6)	51(3)
C(15)	5564(10)	11337(4)	3184(6)	46(3)
C(16)	4706(8)	10700(4)	2994(5)	35(3)
C(17)	53(10)	11894(5)	2151(7)	51(3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

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Supplementary Material Available: For [Fe(Me3L)]ClO_4, tables of complete bond distances (Table S1) and angles (Table S2), anisotropic displacement parameters (Table S3), and hydrogen atom positional parameters (Table S4) (4 pages). Ordering information is given on any current masthead page.

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