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Articles

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Synthesis, Properties, and the Structure of Tetraethylammonium Tris(pyridine-2-thiolato)ferrate(II). An Example of an Exceptionally Short "Bite" of the Ligand

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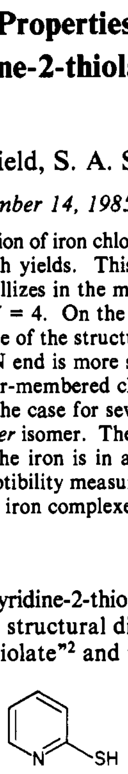
Reaction of iron chlorides with sodium pyridine-2-thiolate in ethanol followed by addition of Et_4NBr affords $(Et_4N)[Fe(SC_5H_4N)_3]$ in high yields. This complex is the first example of a tris chelate of the pyridine-2-thiolato ligand. $(Et_4N)[Fe(SC_5H_6N)_3]$ crystallizes in the monoclinic space group $P2_1/c$ with a = 15.109 (2) Å, b = 9.281 (1) Å, c = 18.627 (2) Å, β = 104.99 (1)°, and Z = 4. On the basis of 4693 unique data ($F_o^2 > 2.5\sigma(F_o^2)$), the structure was refined to R = 5.7%. The most important feature of the structure is the presence of three four-membered chelate rings with an exceptionally small "bite" angle of ca. 66°. The N end is more strongly bound (average Fe–N = 2.152 Å) than the thiolato S end (average Fe–S = 2.575 Å). Formation of four-membered chelate rings produces considerable strain in the ligand framework, which has been discussed and compared with the case for several complexes of other metals containing the pyridine-2-thiolato moiety. The complex is isolated only as the *mer* isomer. The *fac* isomer seems to be unfavorable on steric grounds. Mössbauer studies in the polycrystalline state reveal that the iron is in a +2 oxidation state with a high-spin electronic configuration. Both the UV–vis spectrum and magnetic susceptibility measurements in acetonitrile solution demonstrate octahedral coordination around high-spin Fe(II). Formation of stable iron complexes has been suggested to be one cause for the antifungal activity of pyridine-2-thiol and related compounds.

Introduction

The ligand pyridine-2-thiol (py2SH, **1**) gives rise to an extensive chemistry with structural diversity[1–3] since (i) it can coordinate both in the "thiolate"[2] and the tautomeric "thione" form (**2**),[2,3]



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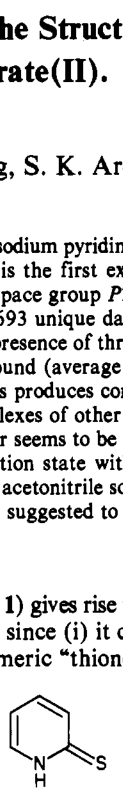

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(ii) it appears as a bridging ligand between two metal centers,[4,5] and, especially, (iii) it generates an exceptionally short "bite" of the ligand when chelated to a metal center.[6–8]

In bis(pyridine-2-thiolato)bis(triphenylphosphine)ruthenium(II), both the pyridine-2-thiolate ligands are bidentate with the S atoms trans to each other.[8] The N–Ru–S angle (67°) and rather long Ru–S bonds demonstrate the structural strains in the molecule because of the formation of four-membered chelate rings. The Fe(II) complexes[3] are, however, reported to be the tetrahedral $FeX_2(LH)_2$ type (X = Cl, Br) where py2SH is coordinated to iron through the "thione" S atom. Since coordination by the thiolato functional group is well documented in Fe(II) chemistry,[9] it is rather surprising that no Fe(II) complex of py2SH is reported where the ligand is bound to the metal center through the pyridine N and thiolato S atoms. We describe in this paper the high-yield syntheses, properties, and structure of tetraethylammonium tris(pyridine-2-thiolato)ferrate(II) (**3**), which is the first octahedral complex of Fe(II) with all three py2SH ligands in the bidentate "thiolate" form. In fact, to our knowledge, **3** is the first example of a true tris(pyridine-2-thiolato)metal(II) complex.

Experimental Section

Preparation of Compounds. Pyridine-2-thiol was procured from Aldrich Chemical Co. and was used without further purification. $FeCl_2\cdot 2H_2O$ was synthesized by following the literature procedure.[10]

In the following two preparations, dry and degassed solvents were used and all manipulations were performed under a pure dinitrogen atmosphere.

$(Et_4N)[Fe(SC_5H_4N)_3]$ from $FeCl_2\cdot 2H_2O$. A solution of 0.82 g (5 mmol) of $FeCl_2\cdot 2H_2O$ in 40 mL of ethanol was slowly added with constant stirring to an ethanolic solution (75 mL) of 17.5 mmol of sodium pyridine-2-thiolate (from 0.40 g of sodium 1.95 g of thiol) whereupon the initial pale yellow color changed to deep orange. Next, 1.15 g (5.5 mmol) of Et_4NBr in 30 mL of ethanol was added to it, and the volume of the orange reaction mixture was reduced to ~60 mL. It was then stored at −20 °C for 4 h. The orange solid, which deposited, was filtered and dried in vacuo. Recrystallization of this solid from warm (~50 °C) acetonitrile afforded large orange blocks, which were collected by filtration after overnight cooling at −20 °C, washed with 1:1 v/v acetonitrile/diethyl ether, and dried in vacuo; 2.0 g (78%) of pure product was obtained. Anal. Calcd for $C_{23}H_{32}N_4FeS_3$: C, 53.48; H, 6.25; N, 10.85; Fe, 10.81. Found: C, 53.13; H, 6.10; N, 10.81; Fe, 10.82.

$(Et_4N)[Fe(SC_5H_4N)_3]$ from $FeCl_3$. An ethanolic solution (100 mL) of 30 mmol of sodium pyridine-2-thiolate (from 0.69 g of sodium and 3.34 g of thiol) was slowly added with stirring to a solution of 0.975 g (6 mmol) of $FeCl_3$ in 40 mL of ethanol. As the addition progressed, the initial yellow mixture turned dark brown and then deep green, and soon a greenish brown precipitate was formed. On further addition of the thiolate solution, the precipitate redissolved and finally a greenish orange solution resulted. The mixture was then filtered, and 1.39 g (6.6 mmol) of Et_4NBr in 30 mL of ethanol was added to the filtrate. Crystallization started almost immediately. After the mixture was cooled at −20 °C for 6 h, the orange solid was collected by filtration and recrystallized from 40 mL of acetonitrile heated initially to 50 °C. The pure product (2.5 g, 80%) was isolated as large orange blocks, which were washed with 1:1 v/v acetonitrile/diethyl ether and dried in vacuo. Anal. Calcd for $C_{23}H_{32}N_4FeS_3$: C, 53.48; H, 6.25; N, 10.85; Fe, 10.81. Found: C, 53.48; H, 6.23; N, 10.72; Fe, 10.82.

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Table I. Summary of Crystal Data and Intensity Collection and Structure Refinement Parameters for $(Et_4N)[Fe(SC_5H_4N)_3]$

formula (mol wt)	$C_{23}H_{32}N_4FeS_3$ (516.56)
a, Å	15.109 (2)
b, Å	9.281 (1)
c, Å	18.627 (2)
β, deg	104.99 (1)
cryst syst	monoclinic
V, Å^3	2523
Z	4
d_{calcd}, g/cm^3	1.365
d_{obsd}, g/cm^3	1.37[a]
space group	$P2_1/c$
crystal dimens, mm	0.21 × 0.20 × 0.39
radiation	Mo Kα (λ = 0.71069 Å)
abs coeff μ, cm^{-1}	9.636
scan speed, deg/min	4–6
2θ limits, deg	$4.0 \leq 2\theta \leq 60.0$
scan range, deg	ω symmetrically over 1.0° about K$\alpha_{1,2}$ max
bkgd/scan time ratio	1.0
no. of data collcd	7348 ($\pm h,+k,+l$)
no. of unique data ($F_o^2 > 2.5\sigma(F_o^2)$)	4693
no. of variables	280
goodness of fit	2.02
R,[b] %	5.7
R_w,[c] %	6.3
temp, K	163

[a] Determined by the neutral buoyancy technique in $ZnCl_2/H_2O$ system. [b] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$.

When the order of addition in the preceding synthesis was reversed, i.e. $FeCl_3$ to thiolate, a dark insoluble precipitate was formed, which was not investigated further.

In the solid state, the compound is moderately sensitive to oxygen. The orange solution in acetonitrile or DMF, however, rapidly turns dark brown on exposure to oxygen.

Physical Measurements. All measurements were performed under strictly anaerobic conditions. The solvents were dried over appropriate drying agents and freshly distilled under dinitrogen prior to use. ^{1}H NMR spectra were recorded on a General Electric 300-MHz GN-300 instrument in CD_3CN (99%, distilled from CaH_2) with Me_4Si as internal standard. Infrared spectra were measured on a Nicolet MX-S FTIR spectrometer. Electronic spectra were monitored either on a Cary Model 14 or a Hitachi 100-80 spectrophotometer. Electrochemical measurements were made with standard Princeton Applied Research instrumentation using a Pt or a glassy-carbon working electrode. Solution magnetic susceptibility was determined by the conventional NMR method using Me_4Si solution,[11] and reference shift differences were measured to ±0.2 Hz by using a 40–50 mM solution of **3** in CD_3CN in coaxial tubes. Solvent susceptibility[12] and diamagnetic corrections[13] were taken from published data. Mössbauer spectra were obtained with a constant-acceleration spectrometer in the temperature range 300–4.2 K. Polycrystalline samples were dispersed in boron nitride powder. Spectra were measured in a zero applied magnetic field and all ^{57}Fe isomer shifts are quoted vs. Fe metal at room temperature. Microanalyses were performed by Galbraith Laboratories, Inc., TN. The % Fe was determined by EDTA titration using variamine blue as indicator.[14]

Collection and Reduction of X-ray Data. Orange blocks of **3** were obtained from slow cooling of an acetonitrile solution. A suitable crystal was sealed in a glass capillary under dinitrogen. Diffraction experiments were performed on a Syntex $P2_1$ diffractometer with graphite-monochromatized Mo Kα radiation and a Syntex LT-1 inert-gas (N_2) low-temperature delivery system. Data were obtained at 163 K. The details of data collection and structure refinement parameters are summerized in Table I. The orientation matrix and unit cell parameters were determined with 25 machine-centered reflections having $10.2 \leq 2\theta \leq 31.4°$. The intensities of check reflections were recorded after every 96 reflections to monitor crystal and instrument stability. Data were corrected for Lorentz and polarization effects, absorption, and decay. The maximum and minimum transmission factors were 84.7% and 82.5% respectively.

Table II. Positional Parameters (×10^4) for $(Et_4N)[Fe(SC_5H_4N)_3]$

atom	x	y	z
Fe	75096 (4)[a]	93714 (13)[a]	14320 (4)[a]
S(1)	7222 (1)	7340 (1)	446 (1)
S(2)	8329 (1)	11413 (1)	930 (1)
S(3)	7759 (1)	10308 (1)	2767 (1)
N(1)	8550 (2)	7749 (3)	1632 (2)
N(2)	6603 (2)	11003 (4)	848 (2)
N(3)	6524 (2)	8558 (4)	2000 (2)
C(1)	8268 (3)	6865 (5)	1038 (2)
C(2)	8813 (3)	5690 (5)	942 (3)
C(3)	9616 (3)	5407 (5)	1471 (3)
C(4)	9900 (3)	6299 (5)	2091 (3)
C(5)	9347 (3)	7458 (5)	2147 (2)
C(6)	7183 (3)	11939 (5)	662 (2)
C(7)	6858 (3)	13236 (5)	281 (3)
C(8)	5926 (3)	13505 (6)	91 (3)
C(9)	5332 (3)	12503 (6)	269 (3)
C(10)	5690 (3)	11285 (5)	653 (3)
C(11)	6798 (3)	9233 (5)	2666 (2)
C(12)	6315 (4)	9016 (6)	3218 (3)
C(13)	5563 (4)	8132 (7)	3056 (3)
C(14)	5277 (3)	7447 (7)	2367 (2)
C(15)	5790 (3)	7687 (5)	1858 (3)
N(4)	8001 (2)	10134 (4)	−1444 (2)
C(16)	7551 (3)	9484 (5)	−2197 (2)
C(17)	7202 (4)	10552 (6)	−2820 (3)
C(18)	7359 (3)	11175 (5)	−1196 (2)
C(19)	6468 (3)	10508 (6)	−1139 (3)
C(20)	8240 (3)	8929 (5)	−872 (2)
C(21)	8958 (3)	7870 (6)	−981 (3)
C(22)	8856 (3)	10964 (5)	−1497 (2)
C(23)	9442 (3)	11514 (7)	−769 (3)

[a] These coordinates have been multiplied by 10^5.

Solution and Refinement of the Structure. Non-hydrogen atomic scattering factors were taken from literature tabulations.[15] Atomic positions for the Fe and S atoms were obtained by the direct-methods program MULTAN and confirmed by Patterson method. The remaining non-hydrogen atoms were located from successive difference Fourier maps. The structure was refined by the least-squares method minimizing the function $\sum w(|F_o| - |F_c|)^2$, where the weight w is defined as $1/\sigma^2(|F_o|)$ and F_o and F_c are the observed and calculated structure factor amplitudes. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located from a difference Fourier map and included in the model but not refined. Unique data used in the refinement and final R factor are given in Table I. Atomic positional parameters are listed in Table II. Selected interatomic distances and angles are presented in Table III. Thermal parameters of the cation and anion (Table S-I), bond distances and angles for the cation (Table S-II), positional parameters for the hydrogens (Table S-III), unweighted least-square planes of the anion (Table S-IV), and the values of $10|F_o|$ and $10|F_c|$ (Table S-V) are included as supplementary material.

Results and Discussion

Since the α- and γ-mercapto derivatives of N-heteroaromatic compounds are capable of tautomerism, py2SH can exist in the thiol (**1**) or thione (**2**) form. Both ultraviolet and infrared spectral studies have demonstrated that in solution py2SH exists in the thione form.[16] Metal complexes containing py2SH coordinated in the thione form exhibit N–H stretches around 3100 cm^{-1} in their infrared spectra.[3] The reaction of $FeCl_2 \cdot 4H_2O$ with py2SH in ethanol was reported to yield high-spin tetrahedral Fe(py2SH)$_2$Cl$_2$, and the presence of a N–H stretch in both the chloride and bromide compounds suggested coordination of py2SH as thione.[3] The reaction mixture in that attempt contained a sufficient amount of hydrochloric acid, and hence the "thiolate"

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Table III. Observed Distances and Angles in $(Et_4N)[Fe(SC_5H_4N)_3]$

Distances (Å)			
Fe–S(1)	2.589 (1)	N(3)–C(15)	1.344 (6)
Fe–S(2)	2.568 (1)	C(1)–C(2)	1.405 (7)
Fe–S(3)	2.568 (1)	C(2)–C(3)	1.376 (6)
Fe–N(1)	2.142 (4)	C(3)–C(4)	1.395 (7)
Fe–N(2)	2.141 (3)	C(4)–C(5)	1.382 (7)
Fe–N(3)	2.173 (4)	C(6)–C(7)	1.418 (6)
S(1)–C(1)	1.734 (4)	C(7)–C(8)	1.383 (7)
S(2)–C(6)	1.744 (4)	C(8)–C(9)	1.391 (8)
S(3)–C(11)	1.732 (5)	C(9)–C(10)	1.371 (7)
N(1)–C(1)	1.352 (6)	C(11)–C(12)	1.420 (8)
N(1)–C(5)	1.358 (5)	C(12)–C(13)	1.371 (8)
N(2)–C(6)	1.341 (6)	C(13)–C(14)	1.397 (8)
N(2)–C(10)	1.358 (5)	C(14)–C(15)	1.389 (8)
N(3)–C(11)	1.354 (6)		
Angles (deg)			
S(1)–Fe–S(2)	106.7 (1)	Fe–N(3)–C(15)	138.4 (3)
S(1)–Fe–S(3)	152.7 (1)	C(1)–N(1)–C(5)	119.6 (3)
S(2)–Fe–S(3)	98.0 (1)	C(6)–N(2)–C(10)	119.5 (3)
S(1)–Fe–N(1)	65.9 (1)	C(11)–N(3)–C(15)	120.0 (3)
S(1)–Fe–N(2)	100.8 (2)	S(1)–C(1)–N(1)	114.2 (3)
S(1)–Fe–N(3)	94.8 (2)	S(2)–C(6)–N(2)	114.3 (3)
S(2)–Fe–N(1)	100.5 (2)	S(3)–C(11)–N(3)	114.5 (3)
S(2)–Fe–N(2)	66.3 (1)	N(1)–C(1)–C(2)	120.1 (3)
S(2)–Fe–N(3)	152.8 (2)	N(1)–C(5)–C(4)	122.8 (3)
S(3)–Fe–N(1)	98.8 (2)	C(1)–C(2)–C(3)	119.6 (4)
S(3)–Fe–N(2)	99.6 (2)	C(2)–C(3)–C(4)	120.3 (4)
S(3)–Fe–N(3)	66.0 (2)	C(3)–C(4)–C(5)	117.5 (3)
N(1)–Fe–N(2)	158.7 (2)	N(2)–C(6)–C(7)	121.0 (3)
N(1)–Fe–N(3)	103.7 (2)	N(2)–C(10)–C(9)	122.3 (3)
N(2)–Fe–N(3)	93.7 (2)	C(6)–C(7)–C(8)	118.6 (3)
Fe–S(1)–C(1)	77.0 (2)	C(7)–C(8)–C(9)	119.7 (4)
Fe–S(2)–C(6)	77.0 (2)	C(8)–C(9)–C(10)	118.9 (3)
Fe–S(3)–C(11)	77.9 (2)	N(3)–C(11)–C(12)	120.4 (3)
Fe–N(1)–C(1)	102.8 (3)	N(3)–C(15)–C(14)	122.7 (3)
Fe–N(1)–C(5)	137.6 (3)	C(11)–C(12)–C(13)	118.5 (4)
Fe–N(2)–C(6)	102.4 (3)	C(12)–C(13)–C(14)	121.1 (4)
Fe–N(2)–C(10)	138.1 (3)	C(13)–C(14)–C(15)	117.4 (4)
Fe–N(3)–C(11)	101.6 (3)		

form of py2SH was not present. In the present report, tetraethylammonium tris(pyridine-2-thiolato)ferrate(II) (3) has been isolated in high yield from the reaction in ethanol of 3.5–5 equiv of preformed thiolate Na(py2S) with iron(II) or iron(III) chloride. This compound is the first example of an octahedral Fe(II) complex where all the three py2SH ligand molecules exist in the thiolate form and are bidentate despite strain in the three four-membered chelate rings. The reaction with $FeCl_2{\cdot}2H_2O$ is clean and straightforward. In the case of $FeCl_3$ as starting material, most probably the first equivalent of thiolate serves as the reducing agent.[9] More than one intermediate species is also involved in the $FeCl_3$ reaction, which is evident from the appearance of different colors and precipitate(s) during the initial stages of mixing. The nature of the intermediate species will be reported elsewhere. Small excess of thiolate in both syntheses serves as oxygen scavenger.

Structure of $(Et_4N)[Fe(SC_5H_4N)_3]$ (3). This compound crystallizes in the $P2_1/c$ space group, and its crystal structure consists of discrete cations and anions. Structural features of the cation are unexceptional and are not considered. The structure of the anion is shown in Figure 1.

The most important feature of the structure of 3 is the presence of *three* four-membered chelate rings. So far, the structures of two complexes, namely bis(pyridine-2-thiolato)bis(triphenylphosphine)ruthenium(II)[6] and dichloro(pyridine-2-thiolato)tin(IV),[17] containing the bidentate pyridine-2-thiolato moiety have been reported. Both structures have the following common features: (a) only *two* pyridine-2-thiolato ligands are present, coordinating through their nitrogen and sulfur atoms such that the sulfur atoms are trans to each other; (b) the structure is distorted octahedral; (c) the N–M–S angle is ~60°; (d) the C–S bond distance (1.73 Å) is considerably larger than that in free py2SH (1.68 Å); (e) the four-membered chelate ring is not strictly coplanar with the pyridine ring, resulting in loss of stabilization energy due to a mesomeric effect. In 3, all of these characteristics are found except for the fact that a third thiolato chelate ring is also present, giving rise to a *mer* isomer. A brief account of the structure of tris(pyridine-2-thiolato)antimony(III)[18] reported that the molecule has a C_3 symmetry (apparently the *fac* isomer, vide infra) and has a Sb–N bond length of 2.830 (7) Å. The ligand molecules were assumed to be bidentate since no N–H stretch in the infrared spectrum was observed. The exceptionally long Sb–N bond distance (the normal Sb(III)–N single bond is 2.53–2.64 Å long[19]) definitely raises the question of whether the ligands could be called bidentate or not. In addition, there is considerable intermolecular Sb–Sb interaction along the molecular C_3 axis in the crystal lattice. Thus, the structure of $[Fe(SC_5H_4N)_3]^-$ is unique among the complexes of py2SH.

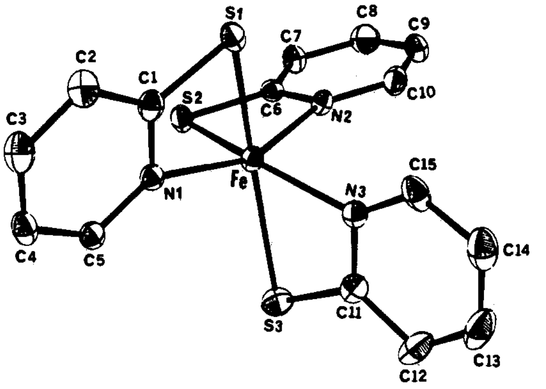

Figure 1. Structure of $[Fe(SC_5H_4N)_3]^-$ (3), showing 50% probability ellipsoids and the atom labeling scheme.

The coordination geometry around Fe in 3 is highly distorted octahedral. The more important bond lengths and bond angles are listed in Table III. The Fe(II)–N bond distances in 3 fall in the narrow range of 2.14–2.17 Å, which are considerably shorter than Fe(II)–N bond lengths in the $[Fe(py)_6]^{2+}$ cation (2.22–2.29 Å),[20] $[Fe(py)_4Cl_2]$ (2.23 Å),[21] or $[Fe(py)_4(SCN)_2]$ (2.24–2.27 Å).[22] The Fe–N(3) bond trans to Fe–S(2) is 0.025 Å longer than the other two Fe–N bonds that are trans to each other. Very few Fe(II)–S_{th} (th = thiolate) distances in high-spin octahedral complexes are reported that could be compared with Fe–S bond lengths in 3. In Fe(II)-bridged double-cubane-type compounds $[M_2Fe_7S_8(SCH_2Ph)_{12}]^{4-}$, the mean Fe(II)–$S_{th}$ distances in the bridge region are 2.567 (6) Å for M = Mo and 2.566 (1) Å for M = W.[23] The Fe–S_{th} bond lengths in 3 are thus comparable to Fe(II)–S_{th} in the double-cubane-type compounds except for the fact that, in the latter, the thiolates connected to Fe(II) are bridging. In tetrahedral thiolato complexes of Fe(II), Fe–S_{th} bond distances lie in the range 2.20–2.37 Å.[9,24] It is, however, expected that formation of a chelate ring would make the Fe–S_{th} bond distance somewhat longer as compared to Fe-S_{th}(terminal, unidentate).[25] This effect might be even more significant in 3 where the four-membered chelate rings produce additional strain. The fact that, in $Ru(SC_5H_4N)_2(PPh_3)_2$, the Ru(II)–N and Ru(II)–S_{th} bonds are found to be respectively shorter and longer than usual

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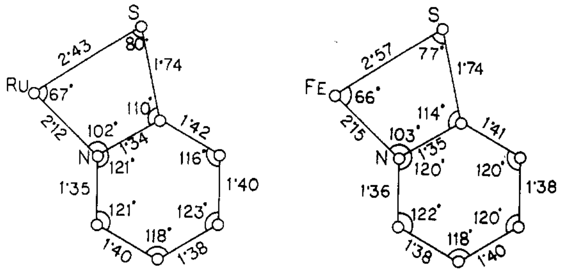

Figure 2. Comparison of (mean) bond lengths and angles in Ru-$(SC_5H_4N)_2(PPh_3)_2$[7] and $(Et_4N)[Fe(SC_5H_4N)_3]$.

Ru(II)–N(py) and Ru(II)–S_{th} bonds prompted the suggestion that the nitrogen is the more strongly bonded of the coordinating atoms in the pyridine-2-thiolato ligand.[7] A similar kind of binding preference is observed with Fe(II) in **3**. It is, however, difficult to determine the relative ratio of the contributions to M–S bond lengthening by the strain in the chelate ring and the inherent weak binding of the thiolato end of $py2S^-$ to M(II).

Formation of a four-membered chelate ring also produces considerable strain in the ligand framework. Thus the Fe–N–C and N–C–S angles are distorted from 120°, expected for sp^2-hybridized atoms, to ~102.5 and ~114.5°, respectively. The Fe–S–C angles are ~77°, as compared with the 90° angle expected if the S centers are using pure p orbitals and the 100–110° range more usually found.

The angles about Fe that show the greatest departure from ideal O_h geometry are the N–Fe–S angles of ca. 66° (Table III). Such short bites have brought N(2) and N(3) (Figure 1) closer (N(2)–Fe–N(3) = 93.7°) as compared to N(1) (N(1)–Fe–N(2) = 158.7°; N(1)–Fe–N(3) = 103.7°) in the FeN_3S plane. The two trans S atoms have also been drawn to each other; the S(1)–Fe–S(3) angle is 152.7° instead of 180°.[26]

The three pyridine planes in **3** are fanned out to some extent to accommodate steric strain. The angles between the py planes (numbered 1–3; Figure 1) are 1–2 = 74.9°, 1–3 = 72.4°, and 2–3 = 97.05°. The deviation of S(1) from plane 1 of the py ring [C(1–5) and N(1)] is 0.06 Å and that of S(2) from plane 2 of the py ring [C(6–10) and N(2)] is 0.05 Å. S(3) lies practically on plane 3 of the py ring [C(11–15) and N(3)]. The dihedral angles between the pyridine and the four-membered chelate rings lie in the narrow range of 1.35–3.0°. Thus the four-membered chelate rings are almost coplanar with the pyridine rings associated with them.

The considerably short C–S bond length in free py2SH (1.68 Å) has been attributed to partial double-bond character (~65%) resulting from the contribution of the tautomeric thione form.[27] In **3**, the C–S bond is longer (1.73 Å) and the C–C bond lengths are very similar (Figure 2). In addition, the C–S bond is not strictly in the plane defined by the ring. These facts indicate that the ligands are coordinated as thiolates with very little contribution from the tautomeric thione form.

Though the unsymmetrical bidentate ligand in **3** leads to the possibility of two geometrical isomer, namely *fac* and *mer*, only the *mer* isomer has been obtained. The possible reason for the preference seems to be a steric one. In complexes containing two bidentate pyridine-2-thiolato fragments, the two S atoms are always trans.[7,16] Burdett[28] has concluded that the most stable geometry for a low-spin d^6 configuration would be *fac*, and this is indeed the case with $[Co(SCH_2CH_2NH_2)_3]$,[29] $[Co(CN)_3(H_2O)_3]$, $[Co(L\text{-}cys)_3]^{3-}$ (cys = cysteine),[29] or even $[Cr(CO)_3(P_4S_3)_3]$.[30] However, the pyridine-2-thiolato complexes $[Co(SC_6H_4N)_3]$ and $[Co(SC_6H_4N)_2(en)]^+$ (en = ethylenediamine) are only isolated as the *mer* isomer.[8] Close inspection of the structure of **3** (Figure 1) reveals that in the *fac* isomer, two pyridine rings will be very close to each other, thus making the configuration energetically unfavorable.

Table IV. Spectroscopic and Electrochemical Data for $(Et_4N)[Fe(SC_5H_4N)_3]$

Electronic Spectrum

solvent	λ_{max}, nm (ϵ, M^{-1} cm^{-1})
MeCN	1440 (7), 940 (11), 460 (1500), 335 (7500)
DMF	1440 (7), 940 (12), 470 (1500), 345 (8500)

Mössbauer Spectrum[a]

T, K	δ,[b,c] mm/s	ΔE_Q,[c] mm/s
230	1.08	2.28
150	1.13	2.81
77	1.18	3.26
4.2	1.19	3.34

Half-Wave Potential[d]

solvent	$E_{1/2}$,[e] V
MeCN	−0.27
DMF	−0.21

[a] In boron nitride matrix. [b] Relative to Fe metal at room temperature. [c] Estimated uncertainties are ±0.03 mm/s in δ and ±0.05 mm/s in ΔE_Q. [d] Cyclic voltammetry, Beckmann Pt-inlay electrode, 0.1 M tetrabutylammonium perchlorate as supporting electrolyte, 50 mV/s scan speed. [e] Values quoted vs. aqueous SCE.

Properties. The high-spin configuration of Fe(II) in **3** has been confirmed by its low-temperature Mössbauer spectrum in the polycrystalline state and magnetic measurements in solution at room temperature. The electronic absorption spectrum of **3** also allows confirmation of the octahedral coordination geometry around Fe(II) in solution. As expected, no N–H stretch has been observed for **3** in its infrared spectrum either in Nujol mull or solution in CS_2.

The only spin-allowed transition in octahedral high-spin Fe(II) complexes, namely $^5T_{2g} \rightarrow {}^5E_g$, appears in the near-infrared region (~1000 nm) and is often split since high-spin Fe^{2+} in both ground and excited states is subjected to Jahn–Teller distortion.[31] In the presence of structural distortion due to strained ligand framework, one need not necessarily invoke the Jahn–Teller effect to explain the splitting. In acetonitrile (Figure 3) and DMF, **3** exhibits a weak (ϵ ~10 M^{-1} cm^{-1}; Table IV) double-humped absorption centered at 1440 and 940 nm. The distortion in the crystal field is reflected in the difference of 500 nm between the two maxima. In tetragonally distorted $[Fe(py)_4Br_2]$, the two peaks appear 1300 and 920 nm respectively.[32] The band at 460 nm responsible for the yellow color of **3** might arise from thiolate-to-metal charge transfer.[33]

The Mössbauer spectral parameters for **3** in the temperature range 4.2–230 K obtained by computer fitting of the experimental spectra with Lorentzian line shapes are collected in Table IV. The spectrum at 4.2 K is displayed in Figure 4. Both the isomer shift δ (1.2 mm/s) and the quadrupole splitting ΔE_Q (3.34 mm/s) are typical of high-spin ferrous ion in a crystal field of low symmetry.[34] Very similar δ and ΔE_Q values have been reported for $[Fe(Chxn)_2(py)_2]$ where Chxn is the cyclohexylxanthate anion.[35] In $[Mo_2Fe_7S_8(SCH_2Ph)_{12}]^{4-}$,[23] the Fe^{2+} center in the bridging region exhibits a similar δ (0.97 mm/s) but rather smaller ΔE_Q (1.95 mm/s) since the effective crystal field around this Fe^{2+} is more symmetric than that in **3**. Variable-temperature studies showed

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(26) S(1)–Ru–S(2) and S(1)–Sn–S(2) are 154.7 (1)°[6] and 154.2 (1)°,[16] respectively.

(27) Penfold, B. R. *Acta Crystallogr.* **1953**, *6*, 707.

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(33) In acetonitrile, py2SH displays two bands centered at 370 nm (ϵ = 6000 M^{-1} cm^{-1}) and 290 (ϵ = 14000 M^{-1} cm^{-1}) nm.

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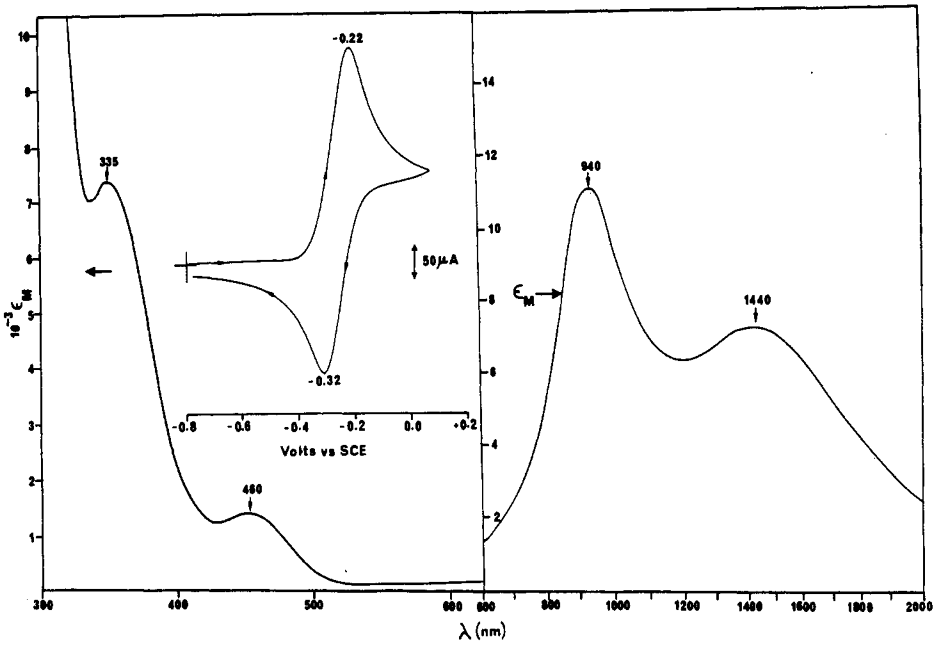

Figure 3. Absorption spectrum of (Et$_4$N)[Fe(SC$_5$H$_4$N)$_3$] (3) in acetonitrile solution. Insert: cyclic voltammogram (50 mV/s) of 3 at the Pt electrode in acetonitrile solution.

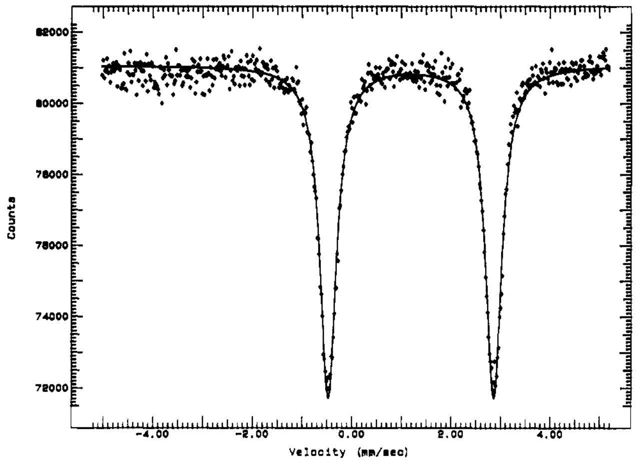

Figure 4. Mössbauer spectrum of polycrystalline (Et$_4$N)[Fe(SC$_5$H$_4$N)$_3$] (3) at 4.2 K. The solid line is a theoretical least-squares fit to the data, assuming Lorentzian line shapes.

that for 3, ΔE_Q remains constant from 4.2 to 77 K but decreases rapidly above 77 K (Table IV). This indicates a low-lying excited state at $E \approx kT = 0.7 \times 100 = 70$ cm^{-1} arising from the splitting of the energy levels of d electrons due to asymmetry in the crystal field and spin–orbit coupling.[36] Magnetic susceptibility measurement in acetonitrile solution at 296 K yields an effective magnetic moment of 5.48 μ_B, which also supports the high-spin ($S = 2$) configuration of Fe(II) in 3.[37]

Cyclic voltammetric studies in acetonitrile and DMF have demonstrated the existence of a one-electron-redox process for 3. A voltammogram recorded at 50 mV/s is shown in Figure 3. The redox system exhibits nearly reversible behavior[38] with $i_c/i_a = 1$ and $\Delta E_p = 100$ mV. Voltammetric characteristics are practically identical on both glassy carbon and Pt electrodes. In DMF, the $E_{1/2}$ value is 60 mV more positive than that in acetonitrile. Though the oxidized species seems to be stable on the voltammetric time scale, no chemical attempts to prepare the oxidation product of 3 have been made.

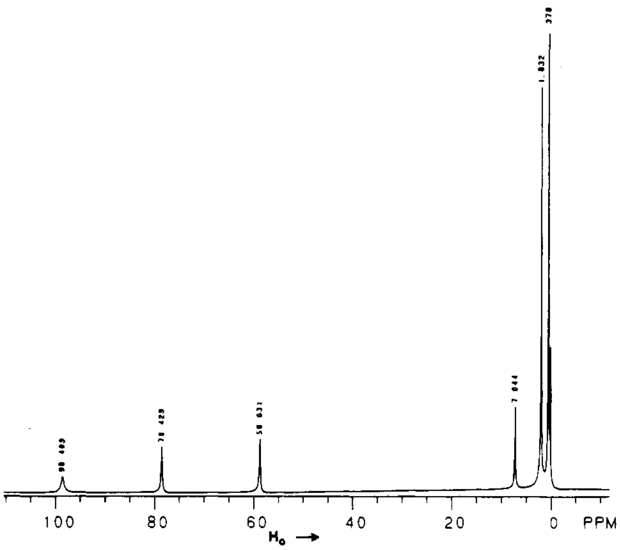

Figure 5. ^{1}H NMR spectrum (300 MHz, ~297 K) of (Et$_4$N)[Fe(SC$_5$H$_4$N)$_3$] (3) in CD$_3$CN.

The ^{1}H NMR spectrum of 3 in CD$_3$CN is shown in Figure 5. The four nonequivalent hydrogens of py2S$^-$ ligands exhibit four distinct and widely separated resonances of equal intensities. The resonances are isotropically shifted as a consequence of the $S = 2$ ground state. Assignment of these resonances by substitution with D or Cl of H on various positions on the py2S$^-$ ligand has not been completed at this time.

Summary

The following points are the principal results and conclusions of this investigation.

(1) The high-yield syntheses of the first "tris" complex (3) of pyridine-2-thiolato ligand have been completed.

(2) The structure of 3 is unique in the sense that it contains three highly strained four-membered chelate rings.

(3) The tris complex is the *mer* isomer. The *fac* isomer seems to be unfavorable due to steric reasons.

(4) Comparisons of the various bond distances and angles in complexes of pyridine-2-thiolato ligands have established a set

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(36) Bancroft, G. M. In *Mössbauer Spectroscopy*; Wiley: New York, 1973; pp 146–150.

(37) (a) The magnetic moments of high-spin Fe^{2+} complexes are usually higher than the spin-only value (4.90 μ_B); e.g., Fe(NH$_3$)$_6$Cl$_2$ has an effective magnetic moment of 5.45 μ_B at room temperature. (b) Earnshaw, A. In *Introduction to Magnetochemistry*; Academic: London, 1968; p 35.

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of structural characteristics in these compounds involving strained coordination.

(5) The various spectroscopic properties of 3 have demonstrated the high-spin configuration of Fe^{2+} ion in a highly distorted octahedral crystal field.

py2SH and related compounds possess antivirial and antifungal activity.[39] Since iron is a necessary nutrient for various microorganisms, the chemistry of the iron complexes of py2SH and related ligands is expected to have other interesting aspects from the unusual structural characteristics discussed in this paper.

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Registry No. $[Et_4N][Fe(SC_5H_4N)_3]$, 102149-44-0.

Supplementary Material Available: Crystal structure data for $(Et_4N)[Fe(SC_5H_4N)_3]$ including thermal parameters of cation and anion (Table S-I), bond distances and angles for the cation (Table S-II), positional parameters for hydrogens (Table S-III), and unweighted least-squares planes of the anion (Table S-IV) (9 pages). Ordering information is given on any current masthead page.

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(39) Coutts, R. T.; Casy, A. F. In *Pyridine and its Derivatives*; Abramovitch, R. A., Ed.; Wiley: New York, 1975; Supplement Part IV, Chapter XVI, p 453.

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Disubstituted Tungstosilicates. 1. Synthesis, Stability, and Structure of the Lacunary Precursor Polyanion γ-$SiW_{10}O_{36}^{8-}$

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The polyanion $SiW_{10}O_{36}^{8-}$ was obtained from β_2-$SiW_{11}O_{39}^{8-}$ at pH 9.1 and isolated as K^+ and Rb^+ salts. The structure of $Rb_8SiW_{10}O_{36}\cdot 10H_2O$ (monoclinic, $P2_1/c$; $a = 12.426$ (3) Å, $b = 19.319$ (6) Å, $c = 19.743$ (5) Å, $\beta = 96.33$ (3)°; $Z = 4$) has been determined and refined to final indices R and R_w of 0.070 and 0.073. The polyanion is a γ isomer, and the ^{183}W NMR spectra of aqueous solutions agree with the solid-state structure. They present one exceptionally weak $^2J_{W-W}$ coupling (4.9 Hz) between corner-sharing tungsten atoms. The polyanion gives 1/1 complexes with alkali-metal and alkaline-earth cations, and its stability in solution is strongly dependent on the formation of these complexes.

Introduction

The analogy between heteropoly oxometalates and metal oxides,[1] from structural and reactivity points of view, has recently attracted much attention.[2] In addition, polysubstituted Keggin-structure heteropolyanions of molybdenum and tungsten with Ti^{IV}, V^V, Nb^V, etc., have enough negative surface charges to bind organometallic transition-metal catalysts.[3] Direct syntheses of these substituted polyanions from constitutive elements always lead to mixtures of isomers.[4] In order to develop stereospecific syntheses of trisubstituted 12-heteropoly compounds, we had prepared the A-type trivacant lacunary polyanions α- and β-$X^NW_9O_{34}^{(14-N)-}$ with $X^N = Si^{IV}, Ge^{IV}, P^V$, and As^V.[5] The reaction of Mo^{VI}, V^V, and Nb^V oxoanions with $SiW_9O_{34}^{10-}$ effectively gives pure α and β forms of $SiW_9Mo_3O_{40}^{4-}$,[5a] $SiW_9V_3O_{40}^{7-}$,[6] and $SiW_9Nb_3O_{40}^{7-}$[3g] polyanions in which the three octahedral molybdenum, vanadium, or niobium atoms are adjacent and share a corner.

Stereospecific syntheses of disubstituted Keggin anions were difficult as there were no bivacant lacunary polyanions available in large amounts until now. The $PW_{10}O_{36}^{7-}$ anion has been described,[7] but experience shows that its preparation is difficult, even in small quantities, as several other polyanions are simultaneously present in the solution. We have studied the conditions of formation of 10-heteropolyanions derived from the Keggin structure and selected the tungstosilicic family because the tungstosilicates are generally more stable than other tungsten heteropolyanions.

Results and Discussion

Formation of the 10-Tungstosilicate. The alkaline hydrolyses of the known tungstosilicates were systematically investigated in order to obtain some information about their specificities and to detect eventual new intermediates. These reactions were studied by polarography, each polyanion being characterized by its oxidation-reduction potentials.[8] The results are summarized in Figure 1.

β-$SiW_{12}O_{40}^{4-}$ only gives β_2-$SiW_{11}O_{39}^{8-}$ at pH 6-8. We have previously shown that, in this polyanion, the lacuna is one of the six equivalent sites adjacent to the tritungstic rotated group of the β structure. Conversely, one can recall that β-$SiW_{12}O_{40}^{4-}$ is

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