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Low-spin iron(III) complexes with N,S coordination: syntheses, structures, and properties of bis(*N*-2-mercaptophenyl-2'-pyridylmethyleniminato)iron(III) tetraphenylborate and bis(*N*-2-mercapto-2-methylpropyl-2'-pyridylmethyleniminato)iron(III) tetraphenylborate

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Abstract

The chemistry of the iron complexes of two Schiff-base ligands namely, *N*-2-mercaptophenyl-2'-pyridylmethylenimine (PyASH, **1**) and *N*-2-mercapto-2-methylpropyl-2'-pyridylmethylenimine (PyMSH, **2**) has been explored in a systematic manner. Use of DMF as solvent allows one to isolate the Fe(II) complexes in pure forms. The Fe(III) complexes [Fe(PyAS)₂]X (X = BF₄, BPh₄ (**3**)) and [Fe(PyMS)₂]BPh₄ (**4**) have been synthesized via oxidation of the corresponding Fe(II) complexes with ferrocenium salts. In **3** and **4**, the deprotonated ligands are coordinated in *mer* fashion with two thiolato S donors *cis* to each other. The deprotonated PyAS⁻ ligand frames in **3** are essentially planar due to extensive electron delocalization. The Fe(III) centers of these two complexes remain low-spin in the temperature range 8–300 K and exhibit rhombic EPR signals with small ($g_{max} - g_{min}$) values. Results of this and other previously reported works suggest that tridentate Schiff-base ligands with N₂S donor set (L) readily afford low-spin Fe(III) centers in [Fe^{III}(L)₂]⁺ complexes. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Iron complexes; Schiff base complexes

1. Introduction

The discovery of a low-spin ($S = \frac{1}{2}$) non-heme [Fe^{III}N₂S₃] center in the enzyme nitrile hydratase [1–6] has raised interest in mononuclear model Fe(III) complexes with N,S coordination. Several groups have structurally characterized Fe(III) complexes with N_xS_y coordination and compared their spectroscopic properties with the biological iron site [7–11]. In such modeling work, it has become apparent that complexes derived from S-containing Schiff bases (chelating ligands with imine nitrogen atoms and thiolato sulfur atoms as donor atoms) comprise low-spin Fe(III) centers [8,11]. The existing literature on Schiff base ligands include few more examples of low-spin Fe(III) complexes with N_xS_y coordination [12,13]. The fact that the redox and reactivity parameters of such complexes provide insight into the function of biological non-heme iron sites warrants new

densation of the amine and mercaptoaldehyde (or ketone) on Fe^{3+} template [8,12,13] since addition of preformed ligands to Fe(III) salts often results in reduction and formation of the Fe(II) complexes and/or S-bridged polymeric species. In general, syntheses of Fe(III) complexes with Fe(III)-S(thiolato) bonds are beset with problems of oligomerization and/ or autoredox reactions generating Fe(II) and RSSR [14,15]. Current methods of synthesizing stable Fe(III)-S(thiolato) bonds include (a) use of sterically hindered thiols and aprotic solvents like DMF [16-19], (b) in situ formation of multidentate ligands with thiolato S donors in the presence of Fe(III) salts [8,12,13], and (c) air oxidation of suitable Fe(II) complexes [7,20]. In this paper, we report two low-spin Fe(III) complexes with N₄S₂ coordination derived from the two Schiff base ligands PyASH (1) and PyMSH (2) where H is the dissociable thiol H. The two complexes $[Fe(PyAS)_2](BPh_4)$ (3) and $[Fe(PyMS)_2](BPh_4)$ (4) have

synthetic procedures that afford these species in pure form and in high yields. To date, most of the low-spin Fe(III)

complexes of Schiff bases have been synthesized via con-

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been synthesized via oxidation of the corresponding Fe(II) complexes with $(Fc^+)(BF_4^-)$ $(Fc^+ = ferrocenium)$ in DMF. The success of this facile and clean oxidative procedure indicates that the method could be used for other Fe(III) complexes with one or more Fe(III)–S(thiolato) bonds. Both **3** and **4** are low-spin in the temperature range 4–300 K.



2. Experimental

2.1. Preparation of compounds

Ferrocenium tetrafluoroborate (Fc⁺)(BF₄⁻), sodium tetraphenylborate, 2-pyridinecarboxaldehyde, and 1-amino-2methyl-2-propanethiol hydrochloride were procured from Aldrich and were used without further purification. Iron-(II)acetate was purchased from Sigma. The ligand 2-(2pyridyl)-benzothiazoline (PyASH in the thiazoline form) was synthesized by the published procedure [21]. All manipulations were performed under an atmosphere of pure and dry dinitrogen. All the iron complexes afforded satisfactory elemental analysis.

2.2. 2-(2-Pyridyl)-4-dimethylthiazolidine

A batch of 2.78 g (19.6 mmol) of 1-amino-2-methyl-2propanethiol hydrochloride was added to a solution of 0.45 g (19.6 mmol) of elemental sodium in 25 ml of degassed methanol. Next, 1.81 ml (19.6 mmol) of 2-pyridinecarboxaldehyde was added and the mixture was heated to reflux for 6 h. The solvent was then removed by rotary distillation and the remaining oil was redissolved in 40 ml of chloroform. The solution was filtered to remove NaCl and washed twice with aqueous solution of NaHCO3 and once with saturated NaCl solution in water. Then the chloroform solution was dried over anhydrous MgSO₄ and evaporated in vacuo. The deep brown oil thus obtained was distilled under reduced pressure. Yield: 3.2 g. (78%). ¹H NMR (CDCl₃, 500 MHz), δ from TMS: 1.49 (s, CH₃), 1.55 (s, CH₃), 2.98 (d, J = 12 Hz, CH), 3.22 (d, J = 12 Hz, CH), 3.9 (NH, br), 5.84 (s, CH), 7.18 (t), 7.23 (d), 7.63 (t), 8.59; ¹³C NMR (CDCl₃, 125.58 MHz), δ from TMS: 28.38, 31.60, 59.50, 66.69, 73.80, 121.89, 122.93, 136.67, 149.77, 158.50.

2.3. $[Fe(PyAS)_2]$

A solution of 1.352 g (6.3 mmol) of 2-(2-pyridyl)-benzothiazoline in 10 ml DMF was added to a slurry of 0.548 g (3.1 mmol) of iron(II) acetate in 10 ml of DMF. A green color developed almost immediately. The mixture was stirred for 24 h when a green precipitate was formed. The volume of the reaction mixture was reduced to 10 ml and the solid was isolated by filtration. Yield: 1.27 g (84%). Selected IR bands (KBr pellet, cm⁻¹): 3048 (m, br), 1591 (m, $\nu_{\rm CN}$), 1575 (s), 1485 (s), 1461 (s), 1445 (s), 1284 (m), 1257 (m), 1150 (m), 1066 (s), 841(m), 758 (s), 738 (s), 656 (m). Electronic absorption spectrum in DMF [$\lambda_{\rm max}$, nm (ϵ , M⁻¹ cm⁻¹): 805 (9 500), 660 (6 900), 450 (16 500).

2.4. $[Fe(PyAS)_2]BF_4$

A solution of 0.72 g (2.63 mmol) of $(Fc^+)(BF_4^-)$ in 5 ml of DMF was slowly added to a solution of 1.27 g (2.63 mmol) of [Fe(PyAS)₂] in 10 ml of DMF and the mixture was stirred continuously. An immediate change in color from green to red occurred and the mixture became homogeneous within a minute. After 30 min, 15 ml of acetonitrile was added to this solution followed by slow addition of 15 ml of dry diethyl ether. The deep red reaction mixture was then filtered and the filtrate was stored first at 4° C for 2 h and then at -20° C for 12 h. The microcrystalline solid which separated during this period was filtered and dried under vacuum. Yield: 920 mg (62%). Selected IR bands (KBr pellet, cm⁻¹): 3060 (m, br), 1600 (m, ν_{CN}), 1580 (m), 1475 (s), 1302 (w), 1260 (m), 1185 (m), 1065 (vs, ν_{BF_4}), 768 (s), 742 (m), 514 (m). Electronic absorption spectrum in DMF $[\lambda_{max}, \text{ nm } (\epsilon, \text{ M}^{-1} \text{ cm}^{-1})]$: 565 (6 500), 430 (8 300). Value of $\mu_{\rm eff}$ (298 K, polycrystalline): 1.95µ_B.

The complex $[Fe(PyAS)_2]BPh_4$ (3) was isolated by slow diffusion of diethyl ether into a solution of $[Fe(PyAS)_2]BF_4$ and NaBPh₄ (5 equiv.) in 1:1 DMF:acetonitrile. This highly crystalline compound was used in the X-ray diffraction work.

2.5. [Fe(PyMS)₂]

To a slurry of 0.632 g (3.63 mmol) of iron(II) acetate in 10 ml of DMF was added a solution of 1.48 g (7.63 mmol) of 2-(2-pyridyl)-4-dimethylthiazolidine in 15 ml DMF and the mixture was stirred continuously. A green color developed within 10 min. The mixture was stirred for 24 h. The volume of the deep green solution was then reduced to 5 ml, and 10 ml of acetonitrile was added to it. The green precipitate thus obtained was filtered, washed with 10 ml of acetonitrile and dried in vacuo. Yield: 1.13 g (72%). Selected IR bands (KBr pellet, cm⁻¹): 2950 (m, br), 1619 (m, $\nu_{\rm CN}$), 1585 (m), 1550 (s), 1470 (m), 1440 (vs), 1370 (m), 1298 (m), 776 (s), 670 (s). Electronic absorption spectrum in DMF [$\lambda_{\rm max}$, nm (ϵ , M⁻¹ cm⁻¹)]: 665 (1700), 580 (1200), 430 (1050).

2.6. $[Fe(PyMS)_2]BPh_4 \cdot MeOH$ (4)

A solution of 0.74 g (2.71 mmol) of $(Fc^+)(BF_4^-)$ in 5 ml of DMF was added to a solution of 1.20 g (2.71 mmol) of [Fe(PyMS)₂] in 10 ml of DMF. The green color immediately changed to red and the reaction mixture became homogeneous within 1 min. After 30 min of stirring, the volume of the reaction mixture was reduced to 5 ml, and 15 ml of methanol was added to it. Dropwise addition of a solution of 1.39 g (4 mmol) of sodium tetraphenylborate in 7 ml of methanol to this red solution resulted in precipitation of the desired complex as a fine powder. The precipitate was collected by filtration and dried in vacuo. Another batch of crystalline product was obtained from the filtrate upon storage at -20° C for 12 h. Total yield: 1.34 g (70%). Selected IR bands (KBr pellet, cm⁻¹): 3050 (s), 1605 (m, $\nu_{\rm CN}$), 1578 (m), 1477 (s), 1426 (m), 1294 (m), 1132 (m), 734 (s), 706 (s), 613 (m). Electronic absorption spectrum in DMF $[\lambda_{\text{max}}, \text{nm} (\epsilon, \text{M}^{-1} \text{ cm}^{-1})]$: 850 (1050), 500 (5500). Value of μ_{eff} (298 K, polycrystalline): 2.20 μ_B .

2.7. X-ray data collection and structure solution and refinement

Black parallelopipeds of 3 were grown by slow diffusion of diethyl ether into a solution of the complex in 1:1 DMF:CH₃CN. Dark red plates of 4 were obtained by slow cooling of a solution of the complex in 3:1 MeOH:DMF. The diffraction data were collected at 130 K. For 3, Mo Ka radiation (graphite monochromator) was employed while Cu Ka radiation (nickel filter) of a rotating anode was used in collecting data for 4. The structure of 3 was solved by the Patterson method. Direct methods were used to solve the structure of 4. Both structures were refined by full-matrix least-squares method (SHELXTL 5, Sheldrick, 1994). Hydrogen atoms bonded to carbon and nitrogen atoms were added geometrically and refined with a riding model. An absorption correction (XABS2) was applied to both data sets [22]. In the final cycles of refinement, all non-hydrogen atoms were refined with anisotropic thermal parameters. Machine parameters, crystal data, and data collection parameters are summarized in Table 1. Selected bond distances and angles are listed in Table 2. The two sets of crystallographic data have been submitted as supplementary material (see Section 4).

2.8. Other physical measurements

Infrared spectra were obtained with a Perkin-Elmer 1600 FTIR spectrophotometer. Absorption spectra were measured on a Perkin-Elmer Lambda 9 spectrophotometer. ¹H and ¹³C NMR spectra were recorded on a Varian 500 MHz Unity Plus instrument. EPR spectra were monitored at X-band frequencies by using a Bruker ESP-300 spectrometer. Room temperature magnetic susceptibility measurements on solid samples were made with a Johnson

Table 1

Summary of crystal data and intensity collection and structure refinement parameters for [Fe(PyAS)₂](BPh₄) (3) and [Fe(PyMS)₂](BPh₄)·MeOH (4)

	3	4	
Formula	C48H38N4S2BFe	C45H50N4OS2BFe	
Molecular weight	801.60	793.67	
Crystal color, habit	black, parallelepiped	dark red, plate	
T (K)	130(2)	123(2)	
Crystal system	triclinic	monoclinic	
Space group	ΡĪ	$P2_1/c$	
a (Å)	8.864(2)	14.269(3)	
b (Å)	14.633(3)	16.687(2)	
<i>c</i> (Å)	16.943(5)	18.189(3)	
α (°)	112.81(2)	90	
β (°)	95.56(2)	108.616(13)	
γ (°)	99.60(2)	90	
$V(Å^3)$	1965.6(8)	4104.5(12)	
Ζ	2	4	
$d_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.354	1.284	
Absorption coefficient $\mu (mm^{-1})$	0.531	4.196	
GOF^{a} on F^{2}	1.012	1.036	
$R1^{b}$ (%)	5.17	7.23	
$wR2^{c}$ (%)	10.41	15.01	

^a GOF = $\left[\sum \{w(F_0^2 - F_c^2)^2\}/(M - N)\right]^{1/2}$ (M = No. of reflections, N = No. of parameters refined).

^b $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$ ^c $wR2 = [\sum \{w(F_o^2 - F_c^2)^2\} / \sum w(F_o^2)^2]^{1/2}$

Matthey magnetic susceptibility balance. Electrochemical measurements were performed with standard Princeton Applied Research instrumentation and a Beckman Pt inlay electrode. Potentials were measured at 25°C versus an aqueous saturated calomel electrode (SCE) as reference.

3. Results and discussion

As expected, the two ligands PyASH (1) and PyMSH (2) are isolated in the thiazoline (1a) and thiazolidine (2a) forms, respectively. The Schiff base forms of these ligands are generated only when metal ions and bases are added to them in polar solvents [21,23-25].



The ligand 1 has been employed previously in the syntheses of complexes of various M2+ ions [23,26-30]. However, no Fe(III) complex of either ligand has been reported so far. In the present work, the Fe(II) complexes of both ligands have been synthesized by reacting Fe(II) acetate

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Table 2						
Selected	bond	distances	(Å)	and	angles (°)

Complex 3			
Fe-N(1)	1.924(3)	Fe-N(2)	2.015(3)
Fe-N(3)	1 997(3)	Fe-N(4)	1.935(3)
Fe-S(1)	2.2228(11)	Fe-S(2)	2 2109(12)
S(1) - C(1)	1 750(3)	S(2) = C(24)	1.751(4)
N(1) - C(7)	1.795(3)	N(1) - C(6)	1.731(4) 1.427(4)
N(1) = C(1) N(2) = C(12)	1.293(4) 1.222(4)	N(1) = C(0) N(2) = C(12)	1.427(4)
N(2) - C(12)	1.332(4)	N(3) = C(13)	1.341(4)
N(4) = C(18)	1.297(4)	N(4) = C(19)	1.41/(4)
C(1) = C(2)	1.395(5)	C(8) = C(9)	1.390(5)
C(14) - C(15)	1.378(5)	C(19) - C(20)	1.394(5)
C(7) - C(8)	1.446(5)	C(17) - C(18)	1.446(5)
B-C(25)	1.642(5)	B-C(31)	1.645(5)
B-C(37)	1.636(5)	B-C(43)	1.644(5)
C(25)-C(26)	1.396(5)	C(31)–C(32)	1.401(4)
C(37)–C(42)	1.395(4)	C(47)–C(48)	1.388(5)
N(1)-Fe-N(2)	81.01(11)	N(1)-Fe-N(3)	98.41(11)
N(1)-Fe- $N(4)$	178.84(11)	N(3)-Fe- $N(2)$	84.21(11)
N(4)-Fe- $N(2)$	100.07(11)	N(4)-Fe- $N(3)$	81.32(11)
N(1) - Fe - S(2)	92.58(8)	N(2)-Fe-S(2)	92.66(8)
N(1) - Fe - S(1)	88 08(8)	N(3)-Fe- $S(1)$	91 13(8)
N(4)-Fe-S(2)	87 78(9)	N(4)-Fe-S(1)	90 79(8)
N(4) = PC = S(2) $N(2) = E_{2} S(1)$	167 26(9)	S(2) = S(1)	90.79(8)
$N(2) = \Gamma C = S(1)$	107.30(8)	S(2) = FC = S(1)	94.20(4)
C(1) - S(1) - Fe	97.10(12)	C(24) - S(2) - Fe	97.20(12)
C(7) = N(1) = C(0)	123.7(3)	C(7) = N(1) = Fe	116.9(2)
C(6)-N(1)-Fe	119.4(2)	C(12) - N(2) - C(8)	118.8(3)
C(13) - N(3) - Fe	127.5(2)	C(17) - N(3) - Fe	112.5(2)
C(18) - N(4) - Fe	116.5(2)	C(19) - N(4) - Fe	119.2(2)
C(2)-C(1)-C(6)	118.6(3)	C(2)-C(1)-S(1)	121.2(3)
C(1)-C(6)-N(1)	115.1(3)	N(1)-C(7)-C(8)	115.8(3)
C(23)-C(24)-S(2)	121.9(3)	C(19)-C(24)-S(2)	119.5(3)
C(37)-B-C(25)	112.9(3)	C(37)-B-C(43)	102.1(2)
C(26)-C(25)-B	123.8(3)	C(30)-C(25)-B	120.8(3)
C(27)-C(26)-C(25)	122.9(3)	C(34)-C(35)-C(36)	120.5(3)
С(48)-С(43)-В	122.8(3)	C(48)–C(47)–C(46)	120.1(3)
Complex 4			
Fe-N(1)	1.928(6)	Fe-N(2)	2.054(6)
Fe-N(3)	1.908(6)	Fe-N(4)	2.030(6)
Fe-S(1)	2.225(2)	Fe–S(2)	2.211(2)
S(1)-C(1)	1.859(7)	S(2)–C(11)	1.861(7)
N(1)-C(2)	1.454(9)	N(1)-C(3)	1.289(9)
N(2)-C(4)	1.375(9)	N(2)–C(8)	1.340(8)
N(3)-C(12)	1.482(9)	N(3)-C(13)	1.274(8)
N(4) - C(14)	1.365(9)	N(4) - C(18)	1.339(9)
C(1)-C(2)	1.504(10)	C(1) - C(9)	1.504(10)
C(1) - C(10)	1.528(10)	C(4) - C(5)	1.367(10)
C(11) - C(19)	1.535(10)	C(11) = C(20)	1.525(10)
C(11) - C(12)	1.532(0)	C(17) - C(18)	1.323(10) 1.373(10)
$P_{C(21)}$	1.552(9) 1.634(10)	C(17) = C(10)	1.575(10) 1.628(10)
D = C(21)	1.034(10)	D = C(39)	1.028(10)
C(21) - C(22)	1.397(9)	C(30) = C(31)	1.394(11)
C(40) - C(41)	1.388(10)	O(1) = C(45)	1.414(10)
N(1)-Fe-N(2)	79.4(2)	N(1)-Fe-N(4)	99.5(2)
N(3)-Fe-N(1)	178.4(3)	N(3)-Fe-N(4)	80.0(2)
N(3)-Fe-N(2)	102.1(2)	N(4)-Fe-N(2)	85.0(2)
N(1)-Fe-S(1)	85.5(2)	N(3)-Fe-S(1)	92.9(2)
N(1)-Fe-S(2)	94.3(2)	N(3)-Fe-S(2)	86.4(2)
N(2)-Fe-S(2)	88.5(2)	N(4) - Fe - S(2)	163.3(2)
N(2) - Fe - S(1)	163.1(2)	N(4) = Fe = S(1)	90.1(2)
S(2) = Fe = S(1)	100.22(8)	C(1) = S(1) = Fe	99.7(2)
$C(11) = S(2) = F_{2}$	102.0(2)	$C(3)_N(1)_{Fe}$	117 8(5)
C(11)-3(2)-1°C	102.0(2)	C(3)-11(1)-1C	117.0(3)

Table 2 (*Continued*)

C(3)–N(1)–C(2)	121.0(6)	C(8)-N(2)-C(4)	118.8(6)	
C(13)-N(3)-C(12)	120.1(6)	C(13)-N(3)-Fe	119.3(5)	
C(12)-N(3)-Fe	119.8(5)	C(9)-C(1)-C(10)	110.5(6)	
C(2)-C(1)-C(9)	110.2(6)	C(2)-C(1)-S(1)	105.6(5)	
N(1)-C(3)-C(4)	117.3(7)	N(2)-C(4)-C(3)	111.9(7)	
C(20)-C(11)-C(12)	112.7(6)	C(20)-C(11)-C(19)	109.6(6)	
N(4)-C(14)-C(13)	113.2(6)	C(39)-B-C(21)	113.1(6)	
C(23)-C(22)-C(21)	123.1(7)	C(27)-C(28)-C(29)	122.5(7)	

with the ligands in anhydrous DMF. The acetate ions promote deprotonation of the Schiff base forms of the ligands in such reactions. Both [Fe(PyAS)₂] and [Fe(PyMS)₂] have been isolated as analytically pure green solids which have been characterized by spectroscopic techniques. Interestingly, when methanol is used as the solvent, addition of Fe(II) acetate to either ligand does not afford the green complex; a black insoluble solid is obtained in the case of PyASH while a blue solution is produced in reactions with PyMSH. In a previous account Garg and Tandon [26], reported the formation of an Fe(II) complex of PyASH in methanol which has the composition $[Fe(PyAS)_2(H_2O)_2]$. The authors suggested that the ligands in this complex are bidentate with the pyridine groups not coordinating. We have found that use of anhydrous DMF does not give rise to any complication and affords the bis complexes [Fe(PyAS)₂] and [Fe(PyMS)₂] as dark green solids. It is important to note that when isolated green [Fe(PyMS)₂] is redissolved in methanol or ethanol, one obtains a blue solution¹. Collectively, these findings suggest that both ligands possibly fail to coordinate in tridentate fashion in alcohols.

The integrity of the Fe(II) complexes in aprotic solvents like DMF (and acetonitrile) is further exemplified by the fact that both [Fe(PyAS)₂] and [Fe(PyMS)₂] can be oxidized to the corresponding Fe(III) species by ferrocenium salts in anhydrous DMF or acetonitrile. The tetraphenylborate salt of both Fe(III) complexes can be isolated as highly crystalline solid although $[Fe(PyAS)_2]^+$ has been isolated with other counter ions $(ClO_4^- \text{ and } BF_4^-)$ as well. The oxidation reaction is clean and can be followed by absorption spectroscopy (vide infra). Since ferrocene, the other product of the reaction, remains soluble in DMF and acetonitrile medium, the isolation of the Fe(III) complexes is quite straightforward. This method of synthesizing [Fe(PyAS)₂](BPh₄) and [Fe(PyMS)₂](BPh₄) is by far the most convenient one; use of air as the oxidant leads to partial decomposition of the complexes (as evident by the absorption spectra) and reactions of Fe(III) salts and ligands invariably lead to in situ reduction and formation of the Fe(II) complexes. Oxidation of $[Fe(PyAS)_2]$ and $[Fe(PyMS)_2]$ to the corresponding Fe(III) complexes could also be achieved by oxidation with (NEt₄)₃[Fe(CN)₆] [31]. However, when one attempts to isolate 3 or 4 from such oxidation reaction, the desired

¹[Fe(PyAS)₂] is insoluble in alcohols.



Fig. 1. Computer-generated thermal ellipsoid (probability level 50%) plot of $[Fe(PyAS)_2]^+$ (cation of 3) with the atom-labeling scheme. Hydrogen atoms are omitted for the sake of clarity.

Fe(III) complex is always contaminated with $(NEt_4)_2$ -[Fe(CN)₆].

3.1. Structure of $[Fe(PyAS)_2]BPh_4$ (3)

The structure of the cation of 3 is shown in Fig. 1 and selected bond distances and angles are listed in Table 2. The coordination geometry around iron is distorted octahedral and the two deprotonated PyAS⁻ ligands are bound in a mer fashion. Both PyAS⁻ frames are essentially planar due to extensive delocalization (Fig. 1). The two imino nitrogen atoms are trans to each other while the two thiolato sulfurs occupy *cis* positions. The average $Fe(III)-S_{thio}$ (thio = thiolate) distance is 2.217(1) Å and is quite typical of Fe(III)-S_{thio} distances (2.21-2.31 Å) observed in complexes of multidentate ligands with one or more thiolato S donor centers [7,11,13,20]. The Fe(III)-N_{imino} distances of 3 (1.924 (3) and 1.935 (3) Å) are practically identical to those of bis(2-aminoethylthiosalicylideneiminato)iron(III) chloride [13] and the Fe(III)– N_{py} (py = pyridine) distances are well within the range of $Fe(III)-N_{py}$ distances noted for other low-spin iron(III) complexes [32,33]. Since all the chelate rings in 3 are five-membered, significant deviations from ideal octahedral geometry are noted in the bond angles S(1)-Fe-N(2) (167.36(8)°) like and N(1)–Fe–N(2) $(81.01(11)^{\circ}).$

3.2. Structure of [Fe(PyMS)₂]BPh₄·MeOH (4)

The structure of the cation of **4** (Fig. 2) is similar to the structure of the cation of **3** (Fig. 1) and the metric parameters are very comparable (Table 2). Here also the geometry around iron is distorted octahedral and the two $PyMS^-$ ligands are bonded to the Fe(III) center in a *mer* fashion. However, the presence of the $-CH_2$ - link between the imine group and the thiolato sulfur in the $PyMS^-$ ligand removes the planarity that one observes in the coordinated $PyAS^-$ ligand frame.



Fig. 2. Computer-generated thermal ellipsoid (probability level 50%) plot of $[Fe(PyMS)_2]^+$ (cation of 4) with the atom-labeling scheme. Hydrogen atoms are omitted for the sake of clarity.

3.3. Oxidation of the Fe(II) complexes by $(Fc^+)(BF_4^-)$

Oxidation of $[Fe(PyAS)_2]$ and $[Fe(PyMS)_2]$ by ferrocenium tetrafluoroborate proceeds smoothly in DMF solution. As shown in Fig. 3, addition of $(Fc^+)(BF_4^-)$ to a solution of $[Fe(PyAS)_2]$ in DMF ($[Fe(PyAS)_2]$ is partially soluble in DMF) brings about a sharp color change of green to red as a result of conversion of $[Fe(PyAS)_2]$ to $[Fe(PyAS)_2]^+$. Also, as the oxidation reaction proceeds, more $[Fe(PyAS)_2]$ dissolves and the reaction goes toward completion quite rapidly. Presence of two isobestic points in the region 650–450 nm indicates the presence of two species, $[Fe(PyAS)_2]$ and $[Fe(PyAS)_2]^+$, in solution. Isolation of the Fe(III) complexes **3** and **4** in high yields from such reaction mixtures suggests that the oxidation reactions are virtually stoichiometric.

When the oxidation is carried out with oxygen instead of ferrocenium salts, the green solutions first turn red and then slowly to deep brown. The absorption spectra indicate that the Fe(III) complexes formed initially, decompose in such reaction mixtures. No Fe(III) complex has been isolated from these reactions.

3.4. Properties

Both [Fe(PyAS)₂] and [Fe(PyMS)₂] are green diamagnetic microcrystalline solids which are moderately sensitive to oxygen. Solutions of these Fe(II) complexes in $(CD_3)_2SO$ exhibit well-resolved NMR spectra, a fact that confirms the low-spin configuration of iron in them. In DMF, [Fe(PyAS)₂] exhibits strong charge transfer bands in the region 700–800 nm (Fig. 3). These absorptions appear in a considerably low energy region due to extensive electronic conjugation in the PyAS⁻ ligand frame. [Fe(PyMS)₂], an analogous complex with less electronic conjugation, exhibits such bands at 550–700 nm.

In the solid state, the two Fe(III) complexes **3** and **4** are indefinitely stable in dry dinitrogen atmosphere. When kept in air, they slowly decompose to brown powders of unknown



Fig. 3. Changes in electronic absorption spectra during oxidation of $[Fe(PyAS)_2]$ to $[Fe(PyAS)_2]^+$ by ferrocenium tetrafluoroborate in DMF. Arrows indicate the direction of growth and decay of the bands of $[Fe(PyAS)_2]$ upon oxidation to $[Fe(PyAS)_2]^+$ by ferrocenium ion.

compositions. In solutions, the complexes are sensitive to both oxygen and moisture.

Kovacs and coworkers have reported two Fe(III) complexes of Schiff base ligands, $[Fe(AMIT)_2]Cl$ and $[Fe(ADIT)_2]Cl$,² which are low-spin at ambient temperature [8]. The Fe(III) complex of the Schiff-base 2-aminoethylthiosalicylideneimine (**5**) is also low-spin at room temperature [13]. In contrast, the Fe(III) complexes of two macrocyclic N₃S₃ ligands reported by Wieghardt and coworkers, exist in an electronic spin equilibrium between the high-spin ($S = \frac{5}{2}$)

$$H_{2N} \xrightarrow{CH_{2}-CH_{2}}_{H_{2}N} = C_{L_{3}} \xrightarrow{SH}_{H_{2}N} \xrightarrow{CH_{2}-CH_{2}}_{H_{2}N} = C_{L_{3}} \xrightarrow{SH}_{CH_{3}-CH_{3}}_{CH_{3}} \xrightarrow{H}_{SH} \xrightarrow{CH_{2}-CH_{3}}_{SH}$$

and low-spin $(S = \frac{1}{2})$ state [7]. At ambient temperature, polycrystalline 3 and 4 exhibit effective magnetic moments of $1.98\mu_B$ and $2.20\mu_B$, respectively. These magnetic moment values confirm that both Fe(III) complexes remain low-spin $(S = \frac{1}{2})$ at room temperature. The low-spin configuration of the Fe(III) centers in 3 and 4 is further confirmed by their EPR spectra at low temperatures. The EPR spectra of 3 and 4 at 100 K are shown in Fig. 4 while the EPR spectrum of 3 at 8 K is displayed in Fig. 5. These spectra demonstrate that the Fe(III) centers remain low-spin $(S = \frac{1}{2})$ at temperatures as low as 8 K. The g values of **3** (2.17, 2.11, and 2.01) and 4 (2.13, 2.09, 2.03) are very similar to those of [Fe(AMIT)₂]Cl and [Fe(ADIT)₂]Cl. The complexes 3, 4, [Fe(AMIT)₂]Cl, and [Fe(ADIT)₂]Cl all exhibit $(g_{\text{max}} - g_{\text{min}})$ values in the range (0.10–0.21) and all four complexes have (a) one axial thiolato S atom in the first coordination sphere and (b) the two thiolato S atoms in the cis configuration. The low-pH form of nitrile hydratase exhibits a $(g_{\text{max}} - g_{\text{min}})$ value of 0.21 [6]. In contrast, low-



Fig. 4. X-band EPR spectra of $[Fe(PyAS)_2]^+$ (top) and $[Fe(PyMS)_2]^+$ (bottom) in DMF glass at 100 K. Spectrometer settings: microwave frequency, 9.43 GHz; microwave power, 13 mW; modulation frequency, 100 kHz, modulation amplitude, 2 G.

spin Fe(III) centers in N_xO_y coordination sphere display $(g_{max} - g_{min})$ values in the range of 0.5–1.4 [6,34]. Small spread of *g* values therefore appears to be a characteristic

 $^{^{2}}$ AMIT = 5-amino-2-methyl-3-azapent-2-ene-1-thiolate; ADIT = 6-amino-2,3-dimethyl-4-azahex-3-ene-2-thiolate.



Fig. 5. X-band EPR spectrum of $[Fe(PyAS)_2]^+$ in DMF glass at 8 K. Spectrometer settings: microwave frequency, 9.43 GHz; microwave power, 13 mW; modulation frequency, 100 kHz, modulation amplitude, 2 G.

of low-spin Fe(III) centers with ligated thiolato S donor atoms.

Six-coordinate Fe(III) Schiff-base complexes with N_xO_y donor sets like $[Fe(N_2O)_2]^+$, $[Fe(N_2O_2)L_2]^+$, $[Fe(N_3O_2)L_]^+$ and $[Fe(N_4O_2)]^+$ are either high-spin ($S = \frac{5}{2}$) or exhibit spin equilibria [35,36]. Even the hexadentate Schiff-base ligands with N_4O_2 donor set do not afford low-spin ($S = \frac{1}{2}$) Fe(III) complexes [37]. Thus, the O-analogs of tridentate Schiffbase ligands like AMITH or **5** give rise to Fe(III) complexes of the type $[Fe(N_2O)_2]^+$ which are either high-spin or exhibit spin equilibria. In contrast, Schiff-base ligands with N_2S donor set like **1**, **2**, AMITH, ADITH, and **5** all afford Fe(III) bis complexes that are low-spin at all temperatures. The change in spin configuration due to replacement of O with S in these ligands indicates stronger interaction between thiolato sulfur and Fe(III) center.

The complex **3** exhibits a reversible one-electron redox process with half-wave potentials $(E_{1/2})$ of -0.13 V (versus SCE) in DMF (Fig. 6). As expected, the same voltammogram is obtained with [Fe(PyAS)₂] when the potential scan is initiated from the negative (reducing) side. The $E_{1/2}$ value



Fig. 6. Cyclic voltammogram of [Fe(PyAS)₂]BPh₄ (**3**) in DMF (0.1 M Et₄NClO₄, Pt electrode, 100 mV/s scan speed). Potentials are quoted vs. aqueous SCE.

of **4** is more negative (-0.51 V versus SCE) and the redox process is quasireversible. In the case of homoleptic thiolates of the type $[\text{Fe}(\text{SR})_4]^-$ and $[\text{Fe}(\text{SAr})_4]^-$, the reduction potentials of alkyl thiolates are more negative than those of the arene thiolates [19]. This trend suggests that the more basic alkyl thiolates provide additional stability to Fe(III) centers. The $E_{1/2}$ values of **3** and **4** support this conclusion. Interestingly, complex **4** also exhibits a quasireversible voltammogram with $E_{1/2}$ at +0.47 V (versus SCE). This redox process is most possibly associated with ligand oxidation. Similar ligand-based oxidation has been observed in electrochemical studies on Fe(III) complexes of N₃S₃ macrocyclic ligands [7].

In summary, the Fe(III) complexes of two Schiff-base ligands namely, $[Fe(PyAS)_2]X$ (X = BF₄, BPh₄) and $[Fe(PyMS)_2]$ BPh₄ have been synthesized via oxidation of the corresponding Fe(II) complexes with ferrocenium salts. The Fe(III) centers of these two complexes remain low-spin in the temperature range 8–300 K. Results of this and other previously reported works suggest that tridentate Schiff-base ligands with N₂S donor set (L) give rise to lowspin Fe(III) centers in $[Fe^{III}(L)_2]^+$ complexes.

4. Supplementary material

Tables of crystal data and intensity collection and refinement parameters, positional coordinates, complete tables of bond distances and angles, H atom coordinates, and anisotropic and isotropic thermal parameters for 3 and 4 (24 pages) are available from the authors upon request.

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