Change in the Spin State of an Fe^{III} Center upon One N-to-O Switch in the Coordination of a 2,6-Pyridinedicarboxamido Unit: The Effect of Methyl Thioether and Methyl Ether Appendages at the Ligand Periphery

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Two ligands bearing the 2,6-pyridinedicarboxamide unit, namely PyPSMeH₂ and PyPOMeH₂, have been used to prepare complexes of Fe^{III} which have been structurally characterised. The potentially pentadentate thioether ligand PyPSMeH₂ affords only the bis complex (Et₄N)[Fe(PyPSMe)₂] (1), irrespective of the metal to ligand ratio, due to the weak affinity of the thioether groups for the Fe^{III} center. In [Fe(PyPSMe)₂]⁻, the two PyPSMe^{2–} ligands bind to the iron center in a *mer* fashion and steric crowding among the pendant thioether groups forces one of the four deprotonated carboxamido moieties to bind to the Fe^{III} center through the carbonyl oxygen, giving rise to an FeN₅O chromophore. The tridentate ligand PyPOMeH₂, in its deprotonated form, also gives rise to a bis complex, (Et₄N)[Fe(PyPOMe)₂] (2), in which the two PyPOMe^{2–} ligands bind to the iron center in a

Introduction

In recent years, coordination of carboxamido nitrogen(s) to iron centers and the spectroscopic, redox and reactivity properties of the resulting complexes have received much interest following the discovery of iron $-N_{amido}$ (N_{amido} = carboxamido N) bonds in nitrogenase^[1] and nitrile hydratase.^[2,3] Initially, this type of coordination was thought to be highly unlikely since Fe^{III} rapidly precipitates out as its hydroxide at much lower pH values than that required for the deprotonation of carboxamido nitrogens.^[4] During the past ten years, however, research by $us^{[5-10]}$ and others^[11-15] has demonstrated that coordination of carboxamido nitrogens to Fe^{III} centers can afford sufficiently stable and isolable complexes. Indeed, coordination of this group results in highly negative $E_{1/2}$ values (up to -1.10 V) indicating that carboxamido nitrogens provide significant stability to iron in the +3 oxidation state.^[7] Furthermore, the majority of Fe^{III} complexes coordinated to one, two, or four carboxamido nitrogens contain low spin Fe^{III} cen-

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mer fashion. In this case, however, less steric crowding among the smaller pendant ether groups allows binding of all four carboxamido nitrogens to the Fe^{III} center in $[Fe(PyPOMe)_2]^-$ giving rise to an FeN₆ chromophore. This one N-to-O switch in donor atom makes the two complexes **1** and **2** very different. While complex **2** is low spin (g = 2.18, 1.94) much like the other reported Fe^{III} bis complexes with two ligated 2,6-pyridinedicarboxamido units, complex **1** is high spin (g = 4.3). The spin flip due to a switch in only one N or O donor atom in these two complexes is unprecedented. The two complexes also exhibit different stability towards water.

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ters.^[7,8,9] In addition, it appears that Fe^{III} complexes with Fe^{III} – N_{amido} bonds are resistant toward hydrolysis despite the common belief that the highly basic carboxamido nitrogens could be readily attacked by water. Collectively, these results indicate that carboxamido nitrogens have a high affinity for Fe^{III} centers and impart stability towards hydrolysis of the resultant complexes.

Coordination of designed ligands with built-in 2,6pyridinedicarboxamido unit (Figure 1) to Fe^{III} centers has resulted in complexes with novel structures and properties.^[5,6,9,11,15] Recent work in this laboratory has afforded a variety of Fe^{III} complexes based on this tridentate moiety in the first coordination sphere.^[5,6,10] For example, coordination of the pentadentate ligand POPyH₄ to Fe^{III} (H represents dissociable amide protons) results in high-spin, seven-coordinate, pentagonal bipyramidal complexes with the entire ligand in the basal plane and with two exogenous axial ligands (structure i, Figure 2).^[6] In contrast, the Fe^{III} complex of the similar pentadentate ligand PyPSH₄ is high spin, five-coordinate with a distorted trigonal bipyramidal geometry due to the steric bulk of the thiolato sulfur (structure ii, Figure 2).^[10] It is interesting to note that the potentially pentadentate ligands Py3PH2 and MePy3PH2 invariably afford six-coordinate bis complexes in which the two ligands are coordinated to the Fe^{III} center through the 2,6-pyridinedicarboxamido moiety with unbound pendant

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Figure 1. Ligands with the 2,6-pyridinedicarboxamide moiety (P stands for the peptide functionality in all abbreviations)

pyridine groups (structure iii, Figure 2).^[5] The Fe^{III} centers in both of these complexes are low spin, much like the Fe^{III} complex of LH₂, namely [FeL₂]⁻, reported by Mukherjee and co-workers.^[11] The failure of the pendant pyridine units to bind to the Fe^{III} centers in these complexes is not related to any steric effect, since Py₃PH₂ gives rise to many [Co(Py₃P)(L)]^{+/0} complexes.^[16] We believe that formation of the bis complex [Fe(Py₃P)₂]⁻ instead of [Fe(Py₃P)(L)]^{+/0} with weak Fe^{III}-py interactions is a result of the high stability derived from coordination of four carboxamido nitrogens.

In order to elucidate the effect(s) of steric hindrance on the mode of coordination of carboxamido nitrogens to Fe^{III} centers and the spin-states of the resulting complexes, we have synthesized additional ligands with the 2,6-pyridinedicarboxamide moiety. The two designed ligands employed in this study are the potentially pentadentate ligand PyPSMeH₂ and the tridentate ligand PyPOMeH₂. Although PyPSMeH₂ is expected to bind to iron much like PyPSH₄, we report here that the deprotonated form, PyPSMe²⁻, coordinates to Fe^{III} in a bis fashion irrespective of the ligand to Fe ratio and in the resulting complex, $(Et_4N)[Fe(PyPSMe)_2]$ (1), all the thioether groups remain unbound. Clearly, thioether sulfur (like pyridine nitrogen) is not a good donor for Fe^{III} and hence PyPSMeH₂ behaves like Py₃PH₂. It is also interesting to note that due to the steric repulsion among the pendant thioether groups in 1, one of the carboxamido groups employs the carbonyl oxygen instead of the carboxamido nitrogen, as a donor atom, resulting in an FeN₅O chromophore. As a result of this Nto-O donor switch around the Fe^{III} center in 1, the complex is high spin, which is in contrast to other similar bis complexes with two bound 2,6-pyridinedicarboxamido units (FeN₆ chromophore and all low spin).^[5,11] In order to further substantiate our hypothesis that the steric repulsion among the pendant thioether groups in 1 is responsible for this N-to-O donor switch, we have also synthesized the bis Fe^{III} complex of the tridentate ligand PyPOMeH₂. The pendant ether groups in (Et₄N)[Fe(PyPOMe)₂] (2) give rise to steric hindrance around the Fe^{III} center much like the crowding in 1. As shown later, the structure of 2 is very similar to that of 1 except for the crucial fact that the extent of the steric repulsion among the pendant ether groups in 2 is slightly less than that among the pendant thioether groups in 1. This allows the four carboxamido nitrogens of the two $PyPOMe^{2-}$ ligands to bind to the Fe^{III} center in 2. Since there is no N-to-O switch, complex 2 is once again low spin much like $[FeL_2]^-$ and $[Fe(Py_3P)_2]^-$.

In this paper, we report (a) the syntheses of complexes 1 and 2, (b) comparisons of the structures of 1 and 2 with other related Fe^{III} complexes with bound 2,6-pyridinedicarboxamide moieties, and (c) studies on spin-flip due to the N-to-O switch in 1 and 2.

Results and Discussion

The potentially pentadentate ligand PyPSMeH₂ was synthesized by following a procedure previously reported by this group.^[17] PyPOMeH₂ was prepared by reacting *o*-anisidine with 2,6-pyridinedicarbonyl dichloride (prepared from 2,6-pyridinedicarboxylic acid and thionyl chloride) in chloroform. Reaction of (Et₄N)[FeCl₄] with PyPSMe²⁻ in DMF



Figure 2. Different structures of Fe^{III} complexes of ligands with the 2,6-pyridinedicarboxamide moiety

afforded the red-brown Fe^{III} complex $(Et_4N)[Fe(PyPSMe)_2]$ (1) in good yield. It is important to note that the bis complex 1 is the only product isolated from this reaction irrespective of the ligand to Fe ratio. Thus when a 1:1 ligand to Fe ratio is used, only half of the iron is complexed by the ligand while the rest remains in solution in the form of $[FeCl_4]^-$. Clearly, the strong preference of the carboxamido nitrogens for Fe^{III}, and the weak affinity of the thioether sulfur for Fe^{III} lead to the formation of 1 as the sole product. The bright red complex $(Et_4N)[Fe(PyPOMe)_2]$ (2) was synthesized in high yield by reacting $(Et_4N)[FeCl_4]$ with two equivalents of PyPOMeH₂ and four equivalents of NaH (both relative to iron) in DMF.

Molecular Structure of (Et₄N)[Fe(PyPSMe)₂] (1)

An X-ray crystallographic study of 1 (Table 1) revealed that the coordination geometry around the Fe^{III} center is distorted octahedral, with two PyPSMe²⁻ units ligated in a mer fashion (Figure 3). Interestingly the Fe^{III}N₅O chromophore consists of two pyridine nitrogens, three deprotonated carboxamido nitrogens, and the carbonyl oxygen of the fourth deprotonated carboxamido moiety. This observed mode of binding of the two PyPSMe²⁻ ligands in 1 is not accidental and has also been noted in the corresponding Co^{III} complex (Et₄N)[Co(PyPSMe)₂] (3).^[17] The last carboxamido nitrogen moiety fails to bind through nitrogen due to the steric repulsion that builds up between the pendant thioether groups as an increasing number of carboxamido nitrogens become ligated to the M^{III} center. To the best of our knowledge, there is no other example of such an N-to-O donor switch in Fe^{III} complexes containing carboxamido group(s). A few examples of N-to-O linkage isomerization have been reported with ruthenium complexes^[18] but these complexes contain neutral and not deprotonated carboxamide unit(s).

Table 1. Summary of crystal data and intensity collection and structure refinement parameters for (Et_4N) [Fe-(PyPSMe)₂]·1.7CH₃CN·Et₂O (1·1.7CH₃CN·Et₂O) and (Et_4N) -[Fe(PyPOMe)₂]·2H₂O (2·2H₂O)

Parameters	$1 \cdot 1.7 \text{CH}_3 \text{CN} \cdot \text{Et}_2 \text{O}$	
Empirical formula	C _{57 40} H _{69 10} FeN _{8 70} O ₅ S ₄	C ₅₀ H ₅₈ FeN ₇ O ₁₀
Molecular weight	1145.00	972.88
a [Å]	18.772(4)	11.0430(13)
b Å	14.548(3)	12.3769(17)
c [Å]	21.297(4)	17.997(2)
α [°]	90	89.039(3)
β ^[°]	90.787(8)	76.953(3)
γ [°]	90	75.930(2)
V[Å ³]	5816(2)	2322.5(5)
Z	4	2
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\overline{1}$
$\rho [g \cdot cm^{-3}]$	1.308	1.391
$T(\mathbf{K})$	91(2)	91(2)
μ , [mm ⁻¹]	0.458	0.393
GOF ^[a] on F ²	1.019	1.024
R ₁ ^[b]	6.76	3.77
R_{w2} ^[c]	14.97	9.04

^[a] GOF = $[\Sigma[w(F_0^2 - F_c^2)^2]/(M - N)]^{1/2}$ (M = number of reflections, N = number of parameters refined). ^[b] $R_1 = \Sigma ||F_0| - |F_c||/\Sigma|F_0|$. ^[c] Rw₂ = $\{\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$.

The Fe^{III}-N_{amido} [av. 2.093(3) Å] and Fe^{III}-N_{py} [av. 2.081(3) Å] bond lengths in **1** are significantly longer than those reported for similar Fe^{III} complexes containing *two* coordinated 2,6-pyridinedicarboxamido moieties in their primary coordination sphere.^[5,11] A close examination of the literature reveals three bis complexes of Fe^{III} that contain the 2,6-pyridinedicarboxamido unit, namely (Et₄N)[FeL₂],^[11] Na[Fe(Py₃P)₂],^[5] and Na[Fe(MePy₃P)₂].^[5] All three complexes consist of an Fe^{III}N₆ chromophore with four deprotonated carboxamido nitrogens in the basal



Figure 3. Thermal ellipsoid plot of $[Fe(PyPSMe)_2]^-$, the anion of 1 (at the 50% probability level); H atoms are omitted for the sake of clarity

plane and two axial pyridine donors. As a result of the strong ligand field of the carboxamido nitrogens, these Fe^{III} complexes are all low spin (vide infra) and exhibit shorter Fe^{III} $-N_{amido}$ [av. 1.961 Å] and Fe^{III} $-N_{py}$ [av. 1.877 Å] bond lengths.^[5,11] Interestingly, the bond lengths of 1 compare well with those noted for high spin (vide infra) Fe^{III} complexes that contain *one* 2,6-pyridinedicarboxamido unit in the primary coordination sphere.^[6,10,15] The C–O bond length of the O-bound carbonyl group [1.286(4) Å] is significantly longer than the C–O bond of the N-bound carbonyl groups [av. 1.236 Å] as a result of coordination of the carbonyl oxygen to the Fe^{III} center. Similarly, the C–N bond of the O-bound carboxamido unit [1.299(4) Å] is, as expected, shorter than the C–N bond of the N-bound carboxamido group [av. 1.336 Å] (Table 2).

Table 2. Selected bond lengths [Å] and angles [°] for $(Et_4N)[Fe(PyPSMe)_2]\cdot 1.7CH_3CN\cdot Et_2O$ ($1\cdot 1.7CH_3CN\cdot Et_2O$) and $(Et_4N)[Fe(PyPOMe)_2]\cdot 2H_2O$ ($2\cdot 2H_2O$)

Complex 1				
Fe-O(4)	2.014(2)	Fe-N(4)	2.111(3)	
Fe-N(5)	2.072(3)	O(1) - C(8)	1.236(4)	
Fe-N(3)	2.077(3)	N(1) - C(8)	1.336(4)	
Fe-N(2)	2.090(3)	O(4) - C(35)	1.286(4)	
Fe-N(1)	2.091(3)	N(6) - C(35)	1.299(4)	
O(4) - Fe - N(5)	75.73(10)	N(5)-Fe-N(4)	74.50(11)	
O(4) - Fe - N(3)	90.39(10)	N(3)-Fe-N(4)	94.25(12)	
N(5) - Fe - N(3)	112.90(11)	N(2)-Fe-N(4)	94.81(11)	
O(4) - Fe - N(2)	115.67(10)	N(1)-Fe-N(4)	99.59(12)	
N(5) - Fe - N(2)	166.85(10)	O(4) - C(35) - N(6)	129.7(3)	
N(3) - Fe - N(2)	74.92(11)	O(4) - C(35) - C(34)	114.3(3)	
O(4) - Fe - N(1)	92.37(10)	N(6) - C(35) - C(34)	115.9(3)	
N(5) - Fe - N(1)	99.07(11)	O(1) - C(8) - N(1)	129.0(3)	
N(3) - Fe - N(1)	147.56(12)	O(1) - C(8) - C(9)	119.8(3)	
N(2) - Fe - N(1)	74.80(11)	N(1) - C(8) - C(9)	111.3(3)	
O(4) - Fe - N(4)	149.29(11)			
Complex 2				
Fe-N(2)	1.8743(12)	Fe-N(2)	1.9842(12)	
Fe-N(5)	1.8757(12)	Fe-N(4)	1.9924(12)	
Fe-N(3)	1.9591(11)	N(1) - C(1)	1.3430(18)	
Fe-N(1)	1.9802(12)	O(1) - C(1)	1.2438(17)	
N(2) - Fe - N(5)	178.14(5)	N(1) - Fe - N(6)	91.06(5)	
N(2) - Fe - N(3)	81.52(5)	N(2)-Fe-N(4)	97.86(5)	
N(5) - Fe - N(3)	96.98(5)	N(5)-Fe-N(4)	81.04(5)	
N(2) - Fe - N(1)	81.01(5)	N(3)-Fe-N(4)	91.12(5)	
N(5) - Fe - N(1)	100.49(5)	N(1)-Fe-N(4)	91.20(5)	
N(3) - Fe - N(1)	162.52(5)	N(6)-Fe-N(4)	162.23(5)	
N(2) - Fe - N(6)	99.89(5)	O(1) - C(1) - N(1)	128.20(13)	
N(5) - Fe - N(6)	81.22(5)	O(1) - C(1) - C(2)	120.41(13)	
N(3)-Fe-N(6)	92.00(5)	N(1) - C(1) - C(2)	111.39(12)	

Molecular Structure of (Et₄N)[Fe(PyPOMe)₂] (2)

The coordination geometry around the Fe^{III} center in $[Fe(PyPOMe)_2]^-$ is distorted octahedral with two PyPOMe²⁻ ligands coordinated in a *mer* fashion (Figure 4). Unlike 1, complex 2 consists of an Fe^{III}N₆ chromophore with two axial pyridine nitrogens and *four* equatorial car-

boxamido nitrogens in its coordination sphere and hence resembles typical bis complexes with bound 2,6-pyridinedicarboxamido units such as $[Fe(Py_3P)_2]^-$. It is interesting to note that by simply decreasing the size of the pendant groups from SMe to OMe at the ligand periphery, a more sterically favorable situation can be created such that all six nitrogens are able to bind to the Fe^{III} center.



Figure 4. Thermal ellipsoid plot of $[Fe(PyPOMe)_2]^-$, the anion of 2 (at the 50% probability level); H atoms are omitted for the sake of clarity.

The Fe^{III}-N_{amido} [av. 1.979(3) Å] and Fe^{III}-N_{py} [av. 1.875(3) Å] bond lengths of **2** are similar to those noted in Fe^{III} complexes with FeN₆ chromophores arising from coordination of *two* 2,6-pyridinedicarboxamido units.^[5,11] However, these bonds are consistently shorter than those in **1** due to the low spin nature of the Fe^{III} center in **2** (vide infra). Furthermore, the octahedral geometry of the N₆ framework in **2** is less distorted than that formed by the N₅O framework in **2**. For example, the N_{py}-Fe-N_{py} and N_{amido}-Fe-N_{amido} angles in **1** (166.85° and 147.56° respectively) are substantially smaller than the corresponding angles in **2** (178.14° and 162.23° respectively, Table 2).

Spectroscopic Properties

Coordination of PyPSMe²⁻ and PyPOMe²⁻ to the Fe^{III} centers is readily indicated by the IR spectra of the complexes. Ligation of the deprotonated carboxamido nitrogens to the metal centers results in a red-shift of the carbonyl stretching frequency (v_{co}) from 1684 cm⁻¹ (in both PyPSMeH₂ and PyPOMeH₂) to 1593 cm⁻¹ in **1** and 1603 cm⁻¹ in **2**. Also, the N–H stretching frequency of the free ligand (\approx 3200 cm⁻¹ for both ligands) is absent in the IR spectra of the iron complexes confirming coordination of the ligands in their deprotonated forms.

The EPR spectrum of 1 in DMF glass at 80K confirms the high spin nature of the Fe^{III} center, displaying a strong signal at g = 4.3 (Figure 5). This is contrary to other bis Fe^{III} complexes with coordinated 2,6-pyridinedicarboxamido units.^[5,11] The Fe^{III} centers in such complexes are exclusively low spin and exhibit axial EPR resonances with g values in the range of 2.19-1.94. This is also true for complex 2. In the same DMF glass, complex 2 exhibits an axial EPR spectrum (g = 2.18, 1.94) typical of a low spin Fe^{III} center (Figure 5). The only difference between the two bis complexes 1 and 2 is the fact that in 1, one of the four carboxamido moieties employs the carbonyl oxygen to bind the Fe^{III} center giving rise to an FeN₅O chromophore. This rather simple N-to-O switch in the donor set causes a spin flip and gives rise to the high spin complex 1. In 2, all six nitrogens from the two 2,6-pyridinedicarboxamido units are bonded to Fe^{III}, and the FeN₆ chromophore is low spin much like the other complexes of a similar kind.^[5,11] To the best of our knowledge, change in the spin state due to only one N-to-O donor switch in otherwise similar complexes of Fe^{III} with carboxamide ligands has not been observed before. It appears that the Fe-O_{carbonyl} interaction exerts a crucial effect on the strong ligand field of the carboxamido nitrogens in these species and just one such interaction can change the overall spin state of the complex. A similar trend in spin state has also been observed in other Fe^{III} complexes that contain Fe-N_{amido} bonds in the presence of Fe-O_{phen} bonds (where phen = phenolato oxygen).^[8]



Figure 5. X-band EPR spectra of 1 (bottom panel) and 2 (top panel) in DMF glass at 80 K; instrument settings: microwave power 13 mW, microwave frequency 9.43 GHz, modulation frequency 100 KHz, modulation amplitude 2 G; selected g values are shown

Complexes 1 and 2 are soluble in a variety of solvents such as DMF and CH₃CN giving deep red-orange solutions. This color arises from strong ligand-to-metal charge transfer (LMCT) absorptions at 450 nm for 1 and 440 nm for 2 (both in DMF). Similar LMCT bands have been observed with analogous iron(III) complexes.^[5,11] Although 1 is stable in aprotic solvents, it decomposes readily in water. The initial red solution loses its color within minutes and free PyPSMeH₂ precipitates from the solution as a white solid. This behavior contrasts sharply with that of other Fe^{III} complexes with FeN₆ chromophores, such as Na[Fe(Py₃P)₂],^[5] Na[Fe(MePy₃P)₂],^[5] and especially complex 2. It is therefore evident that the O-bonded Fe^{III} complex 1 is inherently unstable, presumably due to its high spin nature.

Conclusion

In conclusion, we have synthesized and structurally characterized two new, six-coordinate Fe^{III} complexes that contain the 2,6-pyridinedicarboxamido unit. With the potentially pentadentate thioether ligand PyPSMeH₂, only the bis complex (Et₄N)[Fe(PyPSMe)₂] (1) is obtained irrespective of the ligand to Fe ratio. This strongly suggests that thioether sulfurs are not good donor groups for Fe^{III} in the presence of carboxamido groups. On inspection of the few Fe^{III} complexes with bound thioether groups, it becomes evident that coordination of a thioether sulfur to Fe^{III} occurs only when the thioether group(s) exist between other strong donor groups on the ligand frame.^[19-21] The steric repulsion among the pendant thioether groups in 1 gives rise to an FeN5O coordination sphere in which one carbonyl oxygen binds to the Fe^{III} center. It appears that this subtle N-to-O switch in donor atom results in a high spin Fe^{III} center in 1. In the case of the other Fe^{III} complex $(Et_4N)[Fe(PyPOMe)_2]$ (2), the smaller pendant ether groups allow coordination of all four carboxamido nitrogens resulting in a low spin complex with an FeN₆ chromophore. Collectively, these results indicate that the spin state of an Fe^{III} center coordinated by 2,6-pyridinedicarboxamido moieties can be influenced by simple addition of bulky groups to the ligand periphery. Further modifications to the 2,6-pyridinedicarboxamide ligand frame should enable the preparation of other Fe^{III} complexes with novel structural and spectroscopic properties. Such investigations are currently being performed in this laboratory.

Experimental Section

Physical Measurements: Infrared spectra were recorded with a Perkin–Elmer 1600 FTIR spectrophotometer. Absorption spectra were recorded on a Perkin–Elmer Lambda 9 spectrophotometer. ¹H and ¹³C NMR spectra were recorded at 25 °C on a 500 MHz Varian Unity Plus spectrometer. EPR spectra at X-band frequencies were obtained at 80K with a Bruker ESP-300 spectrometer.

Materials and Methods: All manipulations were carried out using standard Schlenk techniques. 2,6-Pyridinedicarboxylic acid, 2-

(methylthio)aniline, *o*-anisidine, and sodium hydride were purchased from Aldrich and used without further purification. $(Et_4N)[FeCl_4]^{[22]}$ and PyPSMeH₂^[17] were synthesized by following published procedures. 2,6-Pyridinedicarbonyl dichloride was prepared by refluxing 2,6-pyridinedicarboxylic acid in neat thionyl chloride. All solvents were distilled from the appropriate drying agents prior to use: DMF from BaO, CH₃CN from CaH₂, THF from Na/benzophenone, Et₂O from Na, and CHCl₃ from CaCl₂.

Preparation of PyPOMeH₂: A solution of *o*-anisidine (3.79 g, 30 mmol) and Et_3N (5.00 g, 50 mmol) in CHCl₃ (40 mL) was slowly added to a solution of 2,6-pyridinedicarbonyl dichloride (3.11 g, 15 mmol) and Et₃N (5.00 g, 50 mmol) in CHCl₃ (50 mL) at 0 °C. The mixture was stirred at room temperature for 24 h. The resultant red solution was washed with aqueous NaHCO3 and NaCl. The CHCl₃ layer was then dried over MgSO₄, filtered, and the solvent was removed by rotary evaporation to yield a red oil. The oil was triturated with Et₂O (25 mL) to yield a light brown solid (3.75 g, 65% yield). ¹H NMR (500 MHz, CDCl₃): $\delta = 3.95$ (s, 6 H, OCH₃), 7.00 (d, 2 H, ArH), 7.10 (t, 2 H, ArH), 7.15 (t, 2 H, ArH), 8.14 (t, 1 H, ArH), 8.55 (d, 2 H, ArH), 8.61 (d, 2 H, ArH), 10.36 (s, 2 H, NH) ppm. ¹³C NMR (500 MHz, CDCl₃): $\delta =$ 56.14 (OCH₃), 110.54 (ArC), 120.24 (ArC), 121.50 (ArC), 124.55 (ArC), 125.34 (ArC), 127.44 (ArC), 139.56 (ArC), 148.97 (ArC), 149.41 (ArC), 161.15 (C=O) ppm. Selected IR absorption bands (KBr pellet): $\tilde{v} = 3371 \text{ cm}^{-1}$ (s, N–H), 3014 (w), 2979 (w), 1684 (vs, C=O), 1602 (s), 1536 (s), 1488 (s), 1461 (s), 1334 (m), 1291 (m), 1248 (s), 1220 (m), 1175 (w), 1138 (w), 1110 (m), 1070 (m), 1047 (m), 1029 (s), 1000 (w), 947 (w), 925 (w), 890 (w), 845 (w), 790 (w), 758 (w), 702 (w), 671 (s), 594 (w).

(Et₄N)[Fe(PyPSMe)₂] (1): NaH (0.037 g, 1.54 mmol) was added to a solution of PyPSMeH₂ (0.310 g, 0.76 mmol) in DMF (15 mL) and the mixture was stirred until all the NaH had reacted. To the resultant yellow solution was added a solution of (Et₄N)[FeCl₄] (0.120 g, 0.38 mmol) in DMF (2 mL). The resultant dark red solution was stirred for 2 h at 25 °C. The solvent was then removed under vacuum and the residue dissolved in CH₃CN (15 mL) and filtered to remove NaCl. Diethyl ether (7 mL) was added to the CH₃CN filtrate and the resulting solution was stored at -20 °C for 48 h. The dark red crystalline solid thus obtained was collected by filtration and dried under vacuum (0.190 g, 51% yield). Selected IR absorption bands: (KBr pellet): $\tilde{v} = 3049 \text{ cm}^{-1}$ (w), 2983 (w), 2918 (w), 1593 (vs, v_{CO}), 1461 (m), 1438 (w), 1377 (m), 1342 (w), 1144 (w), 1068 (w), 968 (w), 749 (w). Absorption spectrum in DMF: λ_{max} (ε , m⁻¹·cm⁻¹) = 550 nm sh, 450 (7000), 365 (12 000).

(Et₄N)[Fe(PyPOMe)₂] (2): PyPOMeH₂ (0.310 g, 0.82 mmol) was dissolved in DMF (10 mL) and to this was added solid NaH (0.046 g, 1.90 mmol). The mixture was stirred for 20 min and (Et₄N)[FeCl₄] (0.140 g, 0.43 mmol) in DMF (2 mL) was then added. The resultant bright red solution was stirred at 25 °C for 2 h. The solvent was then removed in vacuo and the residue dissolved in CH₃CN (15 mL) and filtered to remove NaCl. To the CH₃CN filtrate was added Et₂O (5 mL) and THF (5 mL) and the solution was stored at -20 °C for three days. The bright red crystalline solid thus obtained was collected by filtration (0.290 g, 73% yield). Selected IR absorption bands: (KBr pellet): $\tilde{v} = 3072 \text{ cm}^{-1}$ (w), 2989 (w), 2943 (w), 1603 (vs, C = O), 1578 (s), 1491 (s), 1458 (m), 1374 (m), 1249 (m), 1156 (w), 1112 (m), 1026 (m), 760 (m), 684 (w). Absorption spectrum in DMF: λ_{max} (ϵ , m⁻¹·cm⁻¹) = 440 nm (6600), 305 (18 000).

X-ray Crystal Structure Analysis: Dark red/brown crystals of (Et_4N) [Fe(PyPSMe)₂]·1.7CH₃CN·Et₂O (1·1.7CH₃CN·Et₂O) were grown from CH₃CN/Et₂O (3:1) at -20 °C. Bright red X-ray quality blocks of $(Et_4N)[Fe(PyPOMe)_2]$ ·2H₂O (2·2H₂O) were grown from CH₃CN/Et₂O/THF (3:1:1) at -20 °C. Diffraction data for both complexes were collected at 90 K on a Bruker SMART 1000 diffractometer using Mo- K_{α} (0.71073 Å) radiation, and an absorption correction was applied in each case. The structures were solved by methods (SHELXS-97). In the direct structure of 1.1.7CH₃CN·Et₂O, there is disorder of one of the terminal groups of the ligand containing C22-S3-C28. This disorder has been omitted in Figure 3 for sake of clarity. Instrument parameters, crystal data, and data collection parameters for 1.1.7CH3CN·Et2O and 2·2H₂O are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

CCDC-187840 (1·1.7CH₃CN·Et₂O) and CCDC-187841 (2·2H₂O) contain the supplementary crystallographic data for this paper. These data may be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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