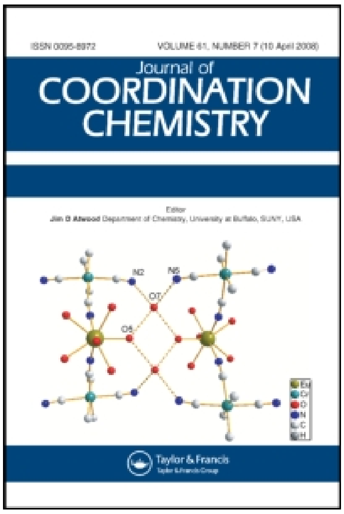

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Syntheses and characterization of new $\mathrm{Mn^{II}}$ and $\mathrm{Fe^{II}}$ complexes with 4'-(4-pyridyl)-2,2' : 6',2''-terpyridine (pyterpy), $[\mathrm{Mn(pyterpy)(MeOH)_2(OAc)}](\mathrm{ClO_4})$ and $[\mathrm{Fe(pyterpy)_2}](\mathrm{SCN})_2 \cdot \mathrm{MeOH}$

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Syntheses and characterization of new Mn^{II} and Fe^{II} complexes with 4′-(4-pyridyl)-2,2′ : 6′,2″-terpyridine (pyterpy), $[Mn(pyterpy)(MeOH)_2(OAc)](ClO_4)$ and $[Fe(pyterpy)_2](SCN)_2 \cdot MeOH$

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Two new Mn^{II} and Fe^{II} complexes with 4′-(4-pyridyl)-2,2′ : 6′,2″-terpyridine (pyterpy), $[Mn(pyterpy)(MeOH)_2(OAc)](ClO_4)$ (**1**) and $[Fe(pyterpy)_2](SCN)_2 \cdot MeOH$ (**2**) have been synthesized and characterized by CHN elemental analysis, IR spectroscopy, and structurally analyzed by single-crystal X-ray diffraction. The thermal stabilities of these compounds were studied by thermal gravimetric (TG) and differential thermal analyses (DTA). The potentially tetradentate pyterpy ligand is a tridentate donor to both Mn(II) and Fe(II). The non-coordinated pyridyl interacts *via* O–H $\cdots$ N and C–H $\cdots$ N hydrogen bonds with adjacent molecules in **1** and **2**, respectively, to form inversion symmetric dimers. Compound **1** is further extended into infinite hydrogen bonded chains *via* pairs of O–H $\cdots$ $O_{acetate}$ hydrogen bonds.

Keywords: Iron(II); Manganese(II); 4′-(4-Pyridyl)-2,2′ : 6′,2″-terpyridine

1. Introduction

Crystal engineering has received considerable interest over the last decade [1–5]. Crystal engineering of supramolecular compounds is usually attained by using bi- or multi-dentate ligands such as pyrazine, 4,4′-bipyridine [6–10], and others to connect metal centers. In general, the type and topology of the product generated from the self-assembly of inorganic metal nodes and organic spacers depends on the ligand [11], the metal valences, and the geometric needs of the metal ions. The topology of polymeric complexes can also be modified by other processes and assembly is complicated and influenced by various factors such as the solvent system [12], template effects, counter

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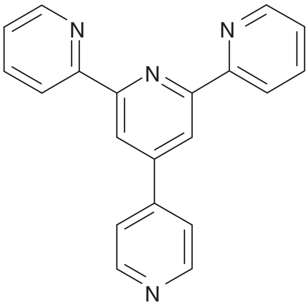
ions, conformational flexibility of the organic ligand, and sometimes the ratio of metal salt and ligand [13, 14].

The ligand 4′-(4-pyridyl)-2,2′ : 6′,2″-terpyridine (pyterpy) is especially interesting because of its multifunctional coordination modes. Recently, different metal complexes with this ligand have been reported [15, 16] with the pyterpy, a tridentate chelating or a mono-tridentate bridging ligand [15]. The pyterpy ligands also have acted as both hydrogen bond acceptors and donors [15b, 16] (scheme 1).

In most of the reported complexes [15] and those reported in this article, the pendant py of the pyterpy ligand is not coordinated and mononuclear complexes are produced. This article focuses on the preparation and description of new Mn^{II} and Fe^{II} complexes with the pyterpy ligand: $[Mn(pyterpy)(MeOH)_2(OAc)](ClO_4)$ (**1**) and $[Fe(pyterpy)_2](SCN)_2 \cdot MeOH$ (**2**).



4'-(4-pyridyl)-2,2':6',2''-terpyridine (pyterpy)

2. Experimental

2.1. *Physical measurements*

The IR spectra were recorded using Perkin–Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O- Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. The thermal behavior was measured with a PL-STA 1500 apparatus. Crystallographic measurements were made using a Bruker Smart APEX area-detector diffractometer. The intensity data were collected using graphite monochromated Mo-Kα radiation. The structures were solved by direct methods and refined by full-matrix least-squares techniques on F^2. Two thiocyanates in **2** are disordered across inversion centers and were refined with bond distances restrained to be the same as those of the nondisordered anion (tables 1 and 2). The methanol solvate and one pyridine are also disordered in a 1 : 1 ratio over two positions. The ADPs of overlapping atoms in all disordered units were set to be identical, the isocyanate carbon atom's ADPs to be close to isotropic, and the ADPs in the disordered pyridine to be similar to each other. The disordered pyridine rings were set to resemble ideal hexagons with bond distances of 1.39 Å and the C–C_{ipso} distances in both units were restrained to be identical. Structure solution and refinement was accomplished using the SHELXTL program package [17]. Molecular structure plots were prepared using ORTEPIII [18a] and Mercury [18b].

Table 1. Crystal data and structure refinement for **1** and **2**.

Identification code	**1**	**2**
Empirical formula	$C_{24}H_{25}ClMnN_4O_8$	$C_{43}H_{32}FeN_{10}OS_2$
Formula weight	587.87	824.76
Temperature (K)	296(2)	100(2)
Wavelength	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	7.6397(14)	8.6108(17)
b	10.2233(18)	10.254(2)
c	16.661(3)	21.451(4)
α	91.106(2)	94.356(3)
β	96.638(2)	95.013(3)
γ	107.071(2)	100.962(3)
Volume (Å^3)	1233.7(4)	1844.0(6)
Z	2	2
D_{Calcd} (g cm^{-3})	1.583	1.485
Absorption coefficient (mm^{-1})	0.702	0.575
Crystal size (mm^{-3})	$0.48 \times 0.35 \times 0.28$	$0.56 \times 20 \times 0.10$
θ range for data collection (°)	2.36–3168	0.96–28.28°
Index ranges	$-10 \le h \le 10$ $-13 \le k \le 13$ $-22 \le l \le 21$	$-11 \le h \le 11$ $-13 \le k \le 13$ $-28 \le l \le 28$
Reflections collected	6074	18838
Independent reflections	5401	9072
Absorption correction	ω scan	ω scan
Max. and min. transmission	0.691 and 0.822	0.944 and 0.617
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6074/2/352	9072/73/539
Goodness-of-fit on F^2	1.019	1.020
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0303$ $wR_2 = 0.0780$	$R_1 = 0.0470$ $wR_2 = 0.1102$
R indices (all data)	$R_1 = 0.0352$ $wR_2 = 0.0816$	$R_1 = 0.0630$ $wR_2 = 0.1224$
Largest different peak and hole (e Å^{-3})	0.515 and −0.420	0.814 and −0.672

Caution! Although no problems were encountered in the preparation of the perchlorate salts, care should be taken during handling of such potentially explosive compounds.

2.2. *Preparation of 4′-(4-pyridyl)-2,2′ : 6′,2″-terpyridine (pyterpy)*

The ligand pyterpy was prepared by a reported method, yielding a white powder, m.p. 227.2–228.1°C; spectroscopic data matched those previously reported [19].

2.3. *Preparation of [Mn(pyterpy)(MeOH)$_2$(OAc)](ClO$_4$) (1)*

4′-(4-Pyridyl)-2,2′ : 6′,2″-terpyridine (pyterpy) (0.154 g, 0.5 mmol), manganese(II) acetate (0.088 g, 0.5 mmol), and sodium perchlorate (0.122 g, 1.0 mmol) were placed in the main arm of the branched tube. Methanol was carefully added to fill the arms, the tube was sealed and the ligand and manganese salt containing arm immersed in an oil

Table 2. Bond lengths (Å) and angles (°) for **1** and **2**.

1		**2**	
Mn1–O8	2.1703(11)	Fe1–N2	1.8739(18)
Mn1–O9	2.2106(11)	Fe1–N6	1.8775(18)
Mn1–N2	2.2823(12)	Fe1–N7	1.9634(19)
Mn1–O2	2.3192(11)	Fe1–N3	1.9663(18)
Mn1–O1	2.3252(11)	Fe1–N5	1.9683(19)
Mn1–N1	2.3283(12)	Fe1–N1	1.9761(18)
Mn1–N3	2.3593(12)	N2–Fe1–N6	176.98(8)
O8–Mn1–O9	177.36(4)	N2–Fe1–N7	100.53(8)
O8–Mn1–N2	91.11(4)	N6–Fe1–N7	80.75(8)
O9–Mn1–N2	87.01(4)	N2–Fe1–N3	80.97(7)
O8–Mn1–O2	84.00(4)	N6–Fe1–N3	101.80(8)
O9–Mn1–O2	98.54(4)	N7–Fe1–N3	89.92(8)
N2–Mn1–O2	151.50(4)	N2–Fe1–N5	97.89(8)
O8–Mn1–O1	93.87(4)	N6–Fe1–N5	80.92(8)
O9–Mn1–O1	86.96(4)	N7–Fe1–N5	161.51(8)
N2–Mn1–O1	152.18(4)	N3–Fe1–N5	91.48(8)
O2–Mn1–O1	56.32(4)	N2–Fe1–N1	80.97(8)
O8–Mn1–N1	90.78(4)	N6–Fe1–N1	96.25(8)
O9–Mn1–N1	86.83(4)	N7–Fe1–N1	93.38(7)
N2–Mn1–N1	70.09(4)	N3–Fe1–N1	161.94(7)
O2–Mn1–N1	137.81(4)	N5–Fe1–N1	90.99(8)
O1–Mn1–N1	82.48(4)		
O8–Mn1–N3	87.70(4)		
O9–Mn1–N3	93.37(4)		
N2–Mn1–N3	69.68(4)		
O2–Mn1–N3	82.06(4)		
O1–Mn1–N3	137.81(4)		
N1–Mn1–N3	139.70(4)		

bath at 60°C while the other arm was kept at ambient temperature. After 5 days, yellow crystals deposited in the cooler arm were filtered off, washed with acetone and ether and air dried (0.191 g, yield 65%), m.p. = 156°C (Found C: 48.61, H: 4.40, N: 9.43, Calcd for $C_{24}H_{25}ClMnN_4O_8$: C: 48.99, H: 4.25, N: 9.52%). IR (KBr) (ν_{max}, cm^{-1}): 3260 (br), 3061 (w), 2950 (w), 1561 (s), 1484 (m), 1400 (s), 1330 (m), 1080 (vs), 950 (m), 750 (m).

2.4. *Preparation of [Fe(pyterpy)$_2$](SCN)$_2$·MeOH (2)*

Complex **2** was prepared via the same method as that used for **1**.

Product 2. Reactant materials: pyterpy (0.154 g, 0.5 mmol), iron(II) acetate (0.089 g, 0.5 mmol), potassium thiocyanate (0.097 g, 1.0 mmol), purple crystals, d.p. 150°C. Yield: 0.290 g, 70% (Found C: 63.10, H: 3.80, N: 16.54, Calcd for $C_{43}H_{32}FeN_{10}OS_2$: C: 62.56, H: 3.88, N: 16.97%). IR (KBr) (ν_{max}, cm^{-1}): 3230 (br), 3066 (w), 2970 (w), 2080 (vs), 1461 (m), 1435 (m), 1330 (m), 895 (m), 755 (m).

^{1}H NMR (DMSO). δ_H: 7.60 (2H, dd, $^3J_{HH} = 4.75$ Hz, $^3J_{HH} = 6$ Hz, $^4J_{HH} = 1$ Hz, arom.); 7.99 (2H, d, $^3J_{HH} = 4.5$ Hz, arom.); 8.08 (2H, dt, $^3J_{HH} = 6$ Hz, $^3J_{HH} = 8$ Hz, $^4J_{HH} = 1.75$ Hz, arom.); 8.72 (2H, d, $^3J_{HH} = 8$ Hz, arom.); 8.78 (2H, d, $^3J_{HH} = 4.75$ Hz, arom.); 8.84 (2H, s, arom.); 8.85 (2H, d, $^3J_{HH} = 4.5$ Hz, arom.) ppm.

^{13}C NMR ($CDCl_3$). δ_C: 29.76, 119.75, 121.69, 122.63, 138.75, 143.95, 148.15, 149.29, 150.62, 153.65, and 156.14 ppm.

3. Results and discussion

4′-(4-Pyridyl)-2,2′ : 6′,2″-terpyridine (pyterpy) and a mixture of manganese(II) acetate and sodium perchlorate or iron(II) acetate and potassium thiocyanate were reacted in methanol. Diffusion along a thermal gradient (the branched tube method) produced $[Mn(pyterpy)(MeOH)_2(OAc)](ClO_4)$ (**1**) and $[Fe(pyterpy)_2](SCN)_2 \cdot MeOH$ (**2**) as yellow and purple crystals, respectively. Both compounds are air-stable and high-melting solids that are soluble in DMSO. The IR spectra of **1** and **2** show absorption bands resulting from the skeletal vibrations of the aromatic rings in the 1400–1600 cm^{-1} range. The absorption bands of the –OH groups of methanol are observed as broad bands centered at 3260 and 3230 cm^{-1} for **1** and **2**, respectively [19]. The IR spectrum of **1** shows ν(COO) vibrations at 1400 and 1561 cm^{-1} and also $\nu(ClO_4)$ at ca 1080 cm^{-1}. The $\Delta(\nu_{as} - \nu_{sym})$ value indicates that the acetate coordinates to Mn^{II} in a bidentate chelating mode [20, 21]. For **2** the characteristic band of the thiocyanate anions appears at 2080 cm^{-1} [22].

The ^{1}H NMR spectrum of the DMSO solution of **2** displays seven distinct resonance signals at 7.60, 7.99, 8.08, 8.72, 8.78, 8.84, and 8.85 ppm assigned to seven different protons of "py" groups of pyterpy and two other signals at 3.10 and 4.10 ppm assigned to lattice methanol. The ^{13}C NMR spectrum of the DMSO solution of **2** displays 11 distinct resonances at 119.75, 121.69, 122.63, 138.75, 143.95, 148.15, 149.29, 150.62, 153.65, and 156.14 ppm assigned to the aromatic carbons of "py" groups and a signal at 29.76 ppm assigned to MeOH. The NMR data of **2** are not significantly different from free pyterpy, indicating that compound **2** breaks up in DMSO solution.

Attempts to isolate 1 : 2 adducts of Mn(II), $[Mn(pyterpy)_2(MeOH)_2(OAc)](ClO_4)$, and 1 : 1 adducts of Fe(II), $[Fe(pyterpy)](SCN)_2 \cdot MeOH$, with different amounts of pyterpy and Mn(II) or Fe(II) salts were not successful; each time the 1 : 1 adduct with Mn(II) and 1 : 2 adduct with Fe(II) was isolated.

Single crystal X-ray diffraction revealed that **1** is a monomeric manganese(II) complex in which the metal is coordinated by one pyterpy ligand, one acetate, and two methanols (figure 1a). The perchlorate is not coordinated to manganese(II). The manganese center is seven coordinate with a "MnN_3O_4" core. The potentially tetradentate ligand 4′-(4-pyridyl)-2,2′ : 6′,2″-terpyridine (pyterpy) is a tridentate donor to Mn(II) in which the nitrogen of the 4-pyridyl ring is not coordinated as previously reported for pyterpy [23, 24]. The monomeric units form π-stacked inversion symmetric dimers with parallel aromatic pyterpy units with separation of the planes of about 3.5 Å (figure 1b). The centroid-to-centroid distance of the terminal 4-pyridyl and the central pyridyl ring of neighboring pyterpy ligands within the polymers is 3.557(2) Å. The dimers are also held together *via* a pair of O–H $\cdots$ N hydrogen bonds between coordinated methanols and the nitrogens of the terminal 4-pyridyl rings with an $N_{pyterpy} \cdots H–O$ distance of 1.914(2) Å (O $\cdots$ N distance is 2.713(2) Å, N $\cdots$ H–O angle 169.4(1)°). The dimers are connected *via* another pair of inversion symmetric hydrogen bonds between the second coordinated methanol molecule and oxygen of acetate to form 1-D infinite chains. The $O_{acetate} \cdots H–O$ distance is 1.836(2) Å, the O $\cdots$ O distance

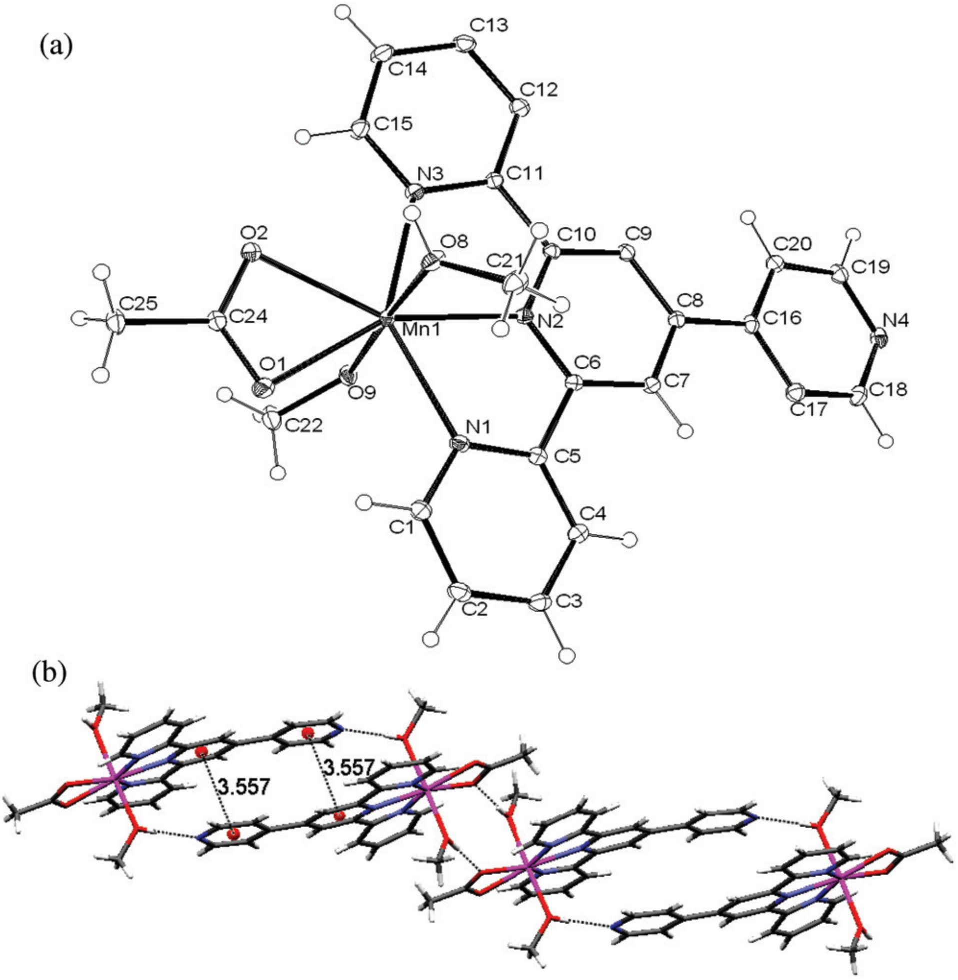


Figure 1. (a) ORTEP view with 30% probability ellipsoids and (b) 1-D chain of **1**.

2.645(2) Å, and the O ⋯ H–O angle is 173.9(1)°. Hydrogen bonding, π-stacking, and part of the 1-D chain of **1** are shown in figure 1(b).

The crystal structure of **2** consists of monomeric units of [Fe(pyterpy)$_2$](SCN)$_2 \cdot$MeOH. Each iron is chelated by nitrogens of two pyterpy ligands in a distorted ocathedron with a "FeN$_6$" core. Thiocyanate and methanol are not coordinated to iron(II) (figure 2a). The pyterpy in **2** only coordinates to iron *via* three nitrogens, similar to **1** and other reported compounds [13, 14]. Monomeric units of **2** are further connected by a pair of weak C–H ⋯ N hydrogen bonds and π–π stacking across an inversion center (figure 2b). There is a hydrogen bond between the disordered pyridine and the disordered methanol with N ⋯ H–O distance of 2.03 Å, the N ⋯ O distance is 2.833(18) Å, and the N ⋯ H–O angle is 159.6(1)°. Individual monomers are almost parallel and the N$_{\text{pyterpy}}$ ⋯ HC bond distances are 2.413(2) Å (with C ⋯ N distance 3.218(2) Å and N ⋯ H–C angle 142.30(2)°) and 2.552(2) Å (with C ⋯ N distance 3.287(2) Å and N ⋯ H–C angle 134.27(2)°). There is π–π stacking between

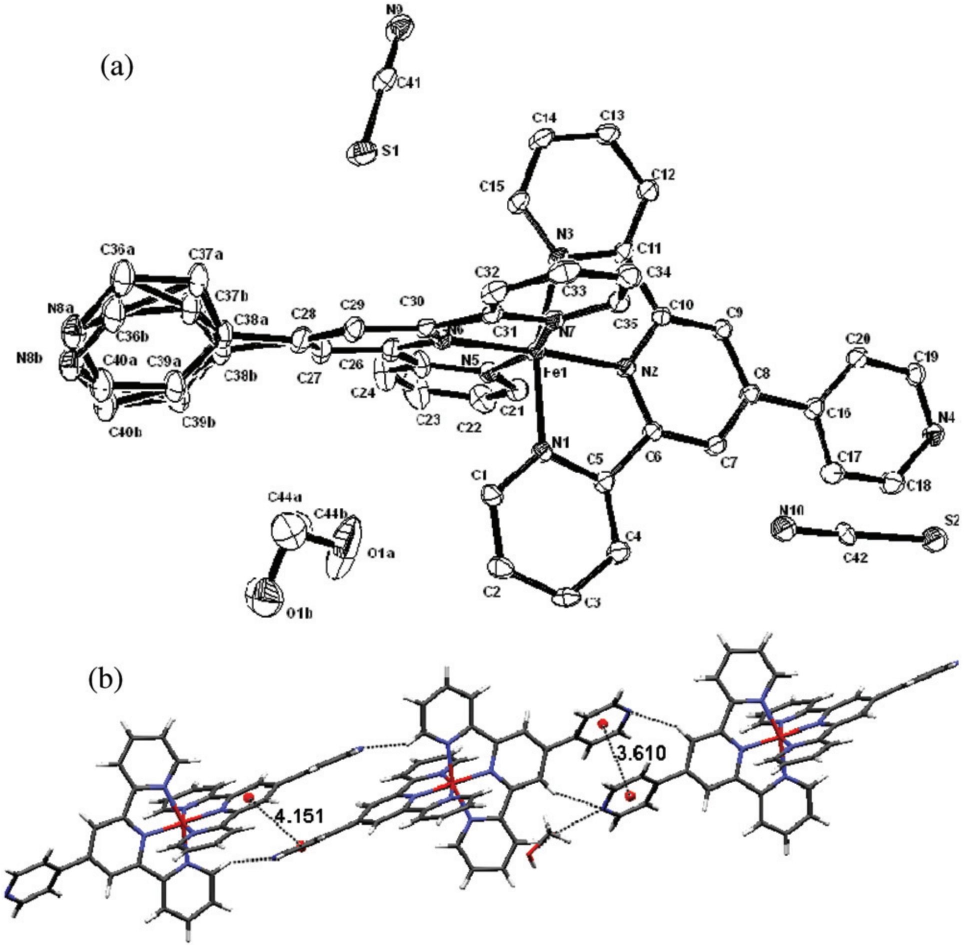


Figure 2. (a) ORTEP view with 30% probability ellipsoids and (b) the 1-D chain formed *via* π–π stacking and CH $\cdots$ N interactions in **2**.

parallel aromatic pyterpy units with centroid-to-centroid distances of 3.610(2) and 4.151(2) Å. Figures 1(b) and 2(b) illustrate that face-to-face interactions between tpy pyridine rings containing N4 in **1** and N4 and N8 in **2** lead to 1-D chains.

A striking similarity between [Mn(pyterpy)(MeOH)$_2$(OAc)](ClO$_4$) and [Fe(pyterpy)$_2$](SCN)$_2$ · MeOH is the π–π stacking between parallel aromatic rings belonging to adjacent chains. The separation of 3.5 Å is close to that of the layers in graphite. Parallel planes of the aromatic moieties indicate that these interactions are "π-stacking", rather than "edge-to-face" or "vertex-to-face". A slightly different intermolecular face-to-face aryl interaction between the pyridine tails is present in **2** with centroid–centroid of 3.610(2) Å. These distances are similar to values recently reported for π–π interactions in divalent transition metal complexes of a terpyridine ligand functionalized at the 4′-position with a biphenyl tail [25, 26]. Thus, the structures of **1** and **2** exhibit dance-type {M(tpy)2} embraces [25, 26], but only in one dimension. However, hydrogen bonding, weak C–H $\cdots$ N secondary interactions, and π–π stacking grow the structure of **2** in 1-D chains (figure 2b).

To examine the thermal stability of **1** and **2**, thermal gravimetric (TG) and differential thermal analyses (DTA) were carried out between 30 and 700°C (Supplementary material). Compound **1** is stable at 155°C where MeOH is lost. The solid residue at 155°C is suggested to be [Mn(pyterpy)(OAc)](ClO_4). At higher temperatures, further decomposition occurs to ultimately give Mn_3O_4 (observed 14.70, Calcd: 13.15%). The DTA curve of **1** indicates the decomposition of the compound takes place with one endothermic effect at 158°C and four exothermic effects at 315, 420, 432, and 525°C (Supplementary material).

Compound **2** is stable at 115°C where it begins to melt (Supplementary material). The TG curve of **2** indicates release of MeOH and decomposition of two pyterpy molecules take place at 425°C in two steps with two endothermic effects at 150 and 290°C as well as one exothermic effect at 410°C. The product at 410°C is probably [Fe$(SCN)_2$], which decomposes upon further heating and the solid residue formed at 600°C is FeS (observed 10.50, Calcd: 10.68%) [27].

4. Conclusion

Two new Mn^{II} and Fe^{II} complexes with the potentially tetradentate 4′-(4-pyridyl)-2,2′ : 6′,2″-terpyridine (pyterpy), [Mn(pyterpy)$(MeOH)_2$(OAc)](ClO_4) (**1**) and [Fe$(pyterpy)_2$]$(SCN)_2 \cdot$MeOH (**2**) have been synthesized and characterized by CHN elemental analysis, IR spectroscopy, and structurally analyzed by X-ray single-crystal diffraction. The thermal stabilities of these compounds were studied by TG and DTA. The potentially tetradentate pyterpy ligand is a tridentate donor in both the complexes. The non-coordinated pyridyl group interacts with hydrogens of adjacent molecules forming hydrogen bonds, extending the monomeric structures into dimeric compounds. Compound **1** is further extended into an infinite hydrogen bonded chain *via* $O\text{–}H \cdots O_{acetate}$ hydrogen bonds.

Supplementary materials

The crystallographic data (excluding structure factors) for **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication number CCDC-685448 and 685449 for **1** and **2**, respectively. Copies of the data can be obtained, free of charge, by application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; Email: data_request@ccdc.cam.ac.uk), or *via* the internet (http://www.ccdc.cam.ac.uk/products/csd/request).

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