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CRYSTAL STRUCTURES OF
[Fe(*m*-NO₂phtpy)₂](ClO₄)₂ AND [Fe(*m*-Clphtpy)₂](ClO₄)₂ (*m*-NO₂phtpy = 4'-(3-nitrophenyl)-
2,2':6',2''-terpyridine and *m*-Clphtpy = 4'-(3-chlorophenyl)-2,2':6',2''-terpyridine)

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Two iron compounds [Fe(*m*-NO₂phtpy)₂](ClO₄)₂ **1** and [Fe(*m*-Clphtpy)₂](ClO₄)₂ **2** are synthesized and their structures are determined by single crystal X-ray diffraction. Crystal data for **1** are: orthorhombic, space group *Pcca*, *a* = 25.471(4) Å, *b* = 10.8182(18) Å, *c* = 14.682(2) Å, and *Z* = 4. Crystal data for **2** are: orthorhombic, space group *Pnma*, *a* = 14.521(2) Å, *b* = 23.980(4) Å, *c* = 23.142(4) Å, and *Z* = 8. The iron atoms are coordinated by six N atoms from two terpyridines in both compounds. These two compounds are all linked by hydrogen bonds with C as donor and O as acceptor into a 3D network for **1** and a 2D network for **2**. If viewed along the *c* direction in **1** and the *a* direction in **2**, both compounds show the ordered figure with terpyridine overlapped as a square and the phenyl rings overlapped as a rectangle or a square.

Keywords: iron(II) compound, 4'-(3-nitrophenyl)-2,2':6',2''-terpyridine, 4'-(3-chlorophenyl)-2,2':6',2''-terpyridine, crystal structure.

INTRODUCTION

2,2':6',2''-Terpyridine (tpy) coordination compounds have been thoroughly studied for their properties, such as photoluminescence, magnetic properties, biological activity, and catalysis [1–4]. Recently, 4'-phenyl terpyridines (phtpy) coordination compounds have been researched well since these terpyridines can be easily synthesized by the Krönke reaction with substituted aromatic aldehydes [5, 6]. The iron compounds of terpyridine (tpy) have often been researched for their crystal structures and electrochemical properties [7–9]. As a result of our investigation of the tpy coordination compounds [10], we report the synthesis and crystal structures of two iron compounds [Fe(*m*-NO₂phtpy)₂](ClO₄)₂ (**1**) and [Fe(*m*-Clphtpy)₂](ClO₄)₂ (**2**) based on newly synthesized 4'-(3-nitrophenyl)-2,2':6',2''-terpyridine and 4'-(3-chlorophenyl)-2,2':6',2''-terpyridine. To the best of our knowledge, this type of 4'-phenyl-2,2':6',2''-terpyridine having a substituent at the *meta*-position of benzene has not been synthesized before and the traditional metal coordination compounds based on this types of tpy have not been synthesized either.

EXPERIMENTAL

Materials and measurements. 4'-(3-Nitrophenyl)-2,2':6',2''-terpyridine and 4'-(3-chlorophenyl)-2,2':6',2''-terpyridine were synthesized by the literature method [5]. 3-Nitrobenzaldehyde and 3-chloro-

Table 1

Crystallographic data for **1** and **2**

	1	2
Complex		
Empirical formula	C ₄₂ H ₂₈ Cl ₂ FeN ₈ O ₁₂	C ₄₂ H ₂₈ Cl ₄ FeN ₆ O ₈
Formula weight	963.47	942.35
Temperature, K	296(2)	291(2)
Wavelength, Å	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>Pcca</i>	<i>Pnma</i>
<i>a</i> , <i>b</i> , <i>c</i> , Å	25.471(4), 10.8182(18), 14.682(2)	14.521(2), 23.980(4), 23.142(4)
α , β , γ , deg.	90, 90, 90	90, 90, 90
Volume, Å ³	4045.6(12)	8059(2)
<i>Z</i>	4	8
Density (calc.), g/cm ³	1.582	1.553
Absorption coefficient, mm ⁻¹	0.583	0.703
<i>F</i> (000)	1968	3840
θ range for data collection, deg.	2.47—21.64	3.91—26.00
Reflections collected	21298	51144
Independent reflections	3559	7896
<i>R</i> _{int}	0.0545	0.0607
Reflection with $I \geq 2\sigma(I)$	2380	5834
Number of parameters	314	552
Goodness-of-fit on <i>F</i> ²	1.046	1.046
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b [$I \geq 2\sigma(I)$]	0.0583, 0.1616	0.0534, 0.1156
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0889, 0.1889	0.0796, 0.1232
Largest diff. peak and hole, e/Å ⁻³	0.571 and -0.527	0.201 and -0.459

$$^a R_1 = \frac{\sum ||F_0| - |F_c||}{\sum |F_0|}$$

$$^b wR_2 = \left[\frac{\sum w(F_0^2 - F_c^2)^2}{\sum w(F_0^2)^2} \right]^{1/2}$$

benzaldehyde were synthesized according to the literature [11]. All the other chemicals were of analytical grade and used as received without further purification. The crystal structure was determined on a Bruker Smart APEX II CCD diffractometer.

Synthesis of [Fe(3-NO₂phtpy)₂](ClO₄)₂ (1). Fe(NH₄)₂(SO₄)₂·6H₂O (19.6 mg, 0.05 mmol) and NaClO₄ (12.2 mg, 0.1 mmol) were dissolved in 5 ml of water and 4'-(3-Nitrophenyl)-2,2':6',2''-terpyridine (35.4 mg, 0.1 mmol) was dissolved in 10 ml of ethanol. The latter was gradually dropped into the former and the solution turned purple immediately and some precipitate appeared. Then some CH₃CN was added to the solution until the precipitate dissolved. The solution was left without disturbance until the purple crystals of **1** suitable for the X-ray diffraction analysis were obtained in two months.

Synthesis of [Fe(3-Clphtpy)₂](ClO₄)₂ (2). Fe(NH₄)₂(SO₄)₂·6H₂O (19.6 mg, 0.05 mmol), 4'-(3-chlorophenyl)-2,2':6',2''-terpyridine (34.4 mg, 0.1 mmol), and NaClO₄ (12.2 mg, 0.1 mmol) were mixed in 10 ml of water-ethanol (v:v, 1:1) and sealed in a 16 ml Teflon-lined stainless steel container, which was heated to 160 °C for 48 h. After gradual cooling to room temperature, the purple block crystals of **2** suitable for the X-ray diffraction analysis were obtained.

X-Ray crystallography. Crystals of **1** and **2** were mounted on a Bruker SMART APEX II CCD diffractometer with graphite monochromated MoK α radiation ($\lambda = 0.071073$ nm) at room temperature.

Table 2

Selected bond lengths (Å) and bond angles (deg.) for **1** and **2**

1		2	
Fe(1)—N(1)	1.885(3)	Fe(1)—N(1)	2.044(2)
Fe(1)—N(2)	1.978(3)	Fe(1)—N(2)	2.016(3)
Fe(1)—N(3)	1.971(3)	Fe(1)—N(3)	2.046(2)
N(1)—Fe(1)—N(2)	80.34(13)	Fe(2)—N(4)	1.916(2)
N(1)—Fe(1)—N(3)	80.90(12)	Fe(2)—N(5)	1.989(2)
		Fe(2)—N(6)	1.993(2)
		N(2)—Fe(1)—N(1)	76.48(10)
		N(1)—Fe(1)—N(3)	75.44(9)
		N(4)—Fe(2)—N(5)	80.42(9)
		N(4)—Fe(2)—N(6)	80.76(9)

Empirical absorption corrections were applied using the SADABS program. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXL-97 program [12, 13]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were generated geometrically. The crystallographic data and structural refinement parameters for compounds **1** and **2** are listed in Table 1. The selected bond lengths and angles are presented in Table 2. Crystallographic data reported in this paper have been deposited at the Cambridge Crystallographic Data Center, CCDC Nos. 885456 for **1** and 912601 for **2**. The data can be obtained free of charge from the Cambridge Crystallographic Data Center, (CCDC), 12 Union Road, Cambridge CB21EZ, UK; (fax: +44-1223-336033; deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

RESULTS AND DISCUSSION

The ORTEP diagram of compound **1** with partial atom labeling is shown in Fig. 1. The center of the Fe ion is coordinated by six N atoms of two 4'-(3-nitrophenyl)-2,2':6',2''-terpyridines. The distances between Fe and N from the central pyridyl rings are 1.885(3) Å, which are shorter than the distances between Fe and N from the outer pyridine rings of 1.971(3) Å and 1.978(3) Å [14–16]. In addition to the difference in bond lengths, the bond angles around Fe are also different and can be divided into two parts: *transoid* angles (176.79(19)° for N1—Fe1—N1ⁱ and 161.22(12)° for N2—Fe1—N3 or N2ⁱ—Fe1—N3ⁱ, symmetry code ⁱ = $-x+1/2, -y+1, z$) and *cisoid* angles ranging from 80.34(13)° to 101.89(13)°. Since the distances and angles are not equal, a distorted octahedral geometry is apparent. The mean deviation of the atoms on tpy from three pyridyl rings is 0.0701 Å, which suggested a plane. These two tpy planes form an angle of 82.80° which slightly deviates from a vertical angle and typical of $[M(\text{tpy})_2]^{2+}$ compounds [17, 18]. The angle formed by the phenyl ring plane and the tpy plane is 32.1°.

In the crystal, there are three types of hydrogen bonds with C atoms as donors and O atoms from nitril or perchlorate anions as acceptors, which are shown in Fig. 2 and listed in Table 3. Two types of hydrogen bonds involving the Cl(2)O₄ anion (C(13)—H(13)⋯O(21) and C(17)—H(17)⋯O(22)) with the bond lengths of 2.40 Å and 2.34 Å result in the 2D layer along the *b* and *c* directions. The third type

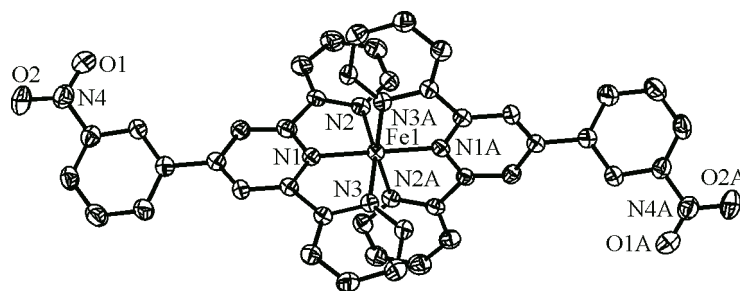


Fig. 1. Perspective view of $[\text{Fe}(3\text{-NO}_2\text{-ptpy})_2]^{2+}$ **1** with thermal ellipsoids at a 30 % level. Hydrogen atoms are omitted for clarity. (Symmetry codes: A: $-x+1/2, -y+1, z$)

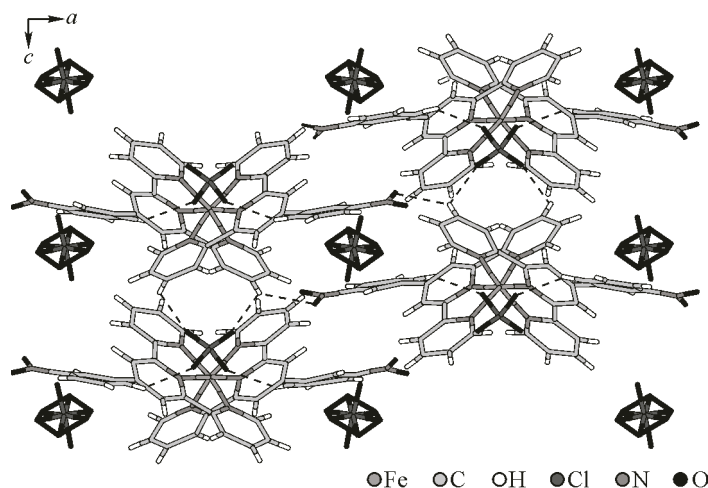


Fig. 2. Hydrogen bonds of **1** indicated by dashed lines viewed along the *b* direction

of the hydrogen bonds C(13)—H(13)···O(1) with the bond length of 2.47 Å interlinks the 2D hydrogen bonded layers into a 3D network.

The ORTEP diagram of compound **2** with partial atom labeling is shown in Fig. 3. Unlike **1**, there are two crystallographically independent Fe ions coordinated by 4'-(3-chlorophenyl)-2,2':6',2''-terpyridine. The distances between Fe1 and the nitrogen atoms from the central pyridyl ring are 2.044(2) Å, which are almost equal to the distance between Fe1 and the nitrogen atoms from the outer pyridyl ring of 2.016(2) Å and 2.046(2) Å, and it is rarely found in $[M(4'\text{-phtpy})_2]^{2+}$ compounds [20]. Three N1—Fe1—N1ⁱ, N2—Fe1—N3 and N2ⁱ—Fe1—N3ⁱ *transoid* angles around Fe1 (symmetry code ⁱ = *x*, $-y+1/2$, $-z+1/2$) are 179.35(14)°, 151.92(10)° and 151.92(10)° respectively, and the other 12 *cisoid* angles range from 75.44(9)° to 105.01(9)°, which shows a distorted octahedral geometry. The angles between two tpy planes (the average deviation of all atoms on the tpy ring is 0.0548 Å) and that be-

Table 3

Hydrogen bonds of **1** and **2**

D—H···A	<i>d</i> (D—H), Å	<i>d</i> (D···A), Å	<i>d</i> (H···A), Å	∠D—H···A, deg.
1				
C(13)—H(13)···O(21)#1	0.93	3.004(10)	2.40	123
C(13)—H(13)···O(1)#2	0.93	3.081(5)	2.47	123
C(17)—H(17)···O(22)#3	0.93	3.179(9)	2.34	151
2				
C(8)—H(7)···O(4)#4	0.93	3.122(4)	2.34	142
C(8)—H(8)···O(3)#4	0.93	3.191(4)	2.54	127
C(13)—H(13)···O(6)	0.93	3.134(4)	2.52	124
C(14)—H(14)···O(3)#5	0.93	3.258(4)	2.48	142
C(30)—H(30)···O(4)#6	0.93	3.358(4)	2.57	143
C(31)—H(31)···O(1)#6	0.93	3.051(4)	2.27	141
C(33)—H(33)···O(3)#5	0.93	3.180(4)	2.42	138

Symmetry codes: #1: $x-1, -y+2, z+1/2$; #2: $x+1/2, -y, -z+3/2$; #3: $-x+3/2, -y+2, z+1$; #4: $x+1, -y+1/2, -z+3/2$; #5: $-x-1/2, -y-1/2, z-1/2$; #6: $x, -y+1/2, -z+3/2$.

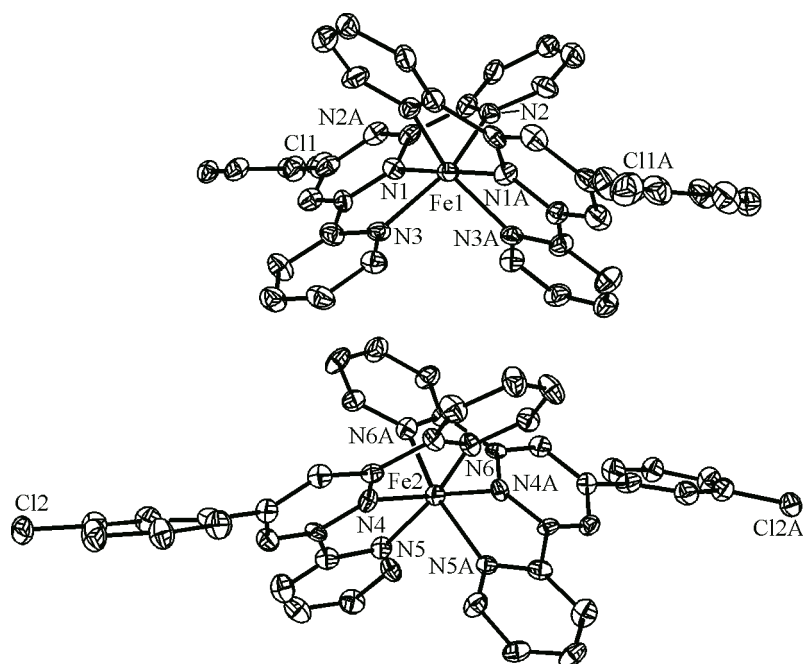


Fig. 3. Perspective view of $[\text{Fe}(\text{3-Cl-phtpy})_2]^{2+} \cdot 2$ with thermal ellipsoids at a 30 % level. Hydrogen atoms are omitted for clarity. (Symmetry codes: A: $x, -y+1/2, -z+1/2$)

tween the phenyl ring and the tpy plane are 79.35° and 36.4° respectively. The distances between Fe2 and the nitrogen atoms from the central pyridyl ring are $1.916(2) \text{ \AA}$, which are slightly shorter than the distance between Fe2 and the nitrogen atoms from the outer pyridyl ring, which are $1.989(2) \text{ \AA}$ and $1.993(2) \text{ \AA}$, and this is similar to other distances in tpy iron compounds [21, 22]. Three *transoid* angles N4-Fe1-N4^i , N5-Fe1-N6 , and $\text{N5}^i\text{-Fe1-N6}^i$ around Fe2 (symmetry code $^i = x, -y+1/2, -z+1/2$) are $179.31(14)^\circ$, $161.07(9)^\circ$, and $161.07(9)^\circ$ respectively, and the other 12 *cisoid* angles range from $80.42(9)^\circ$ to $100.07(9)^\circ$, which also shows a distorted octahedral geometry. The angles between two tpy planes (the average deviation of all atoms on the tpy ring is 0.0529 \AA) and that between the phenyl ring plane and the tpy plane are 81.67° and 35.7° respectively.

There are seven hydrogen bonds of the $\text{C-H}\cdots\text{O}$ types, as shown in Fig. 4 and listed in Table 3. The Cl(4)O_4 anion was only linked to a dication by the $\text{C(13)-H(13)}\cdots\text{O6}$ hydrogen bond with a

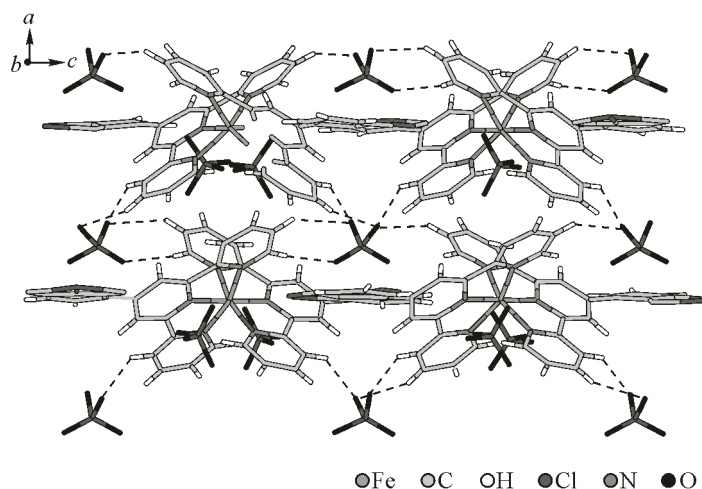


Fig. 4. Hydrogen bonds of **2** indicated by dashed lines viewed along the b direction

length of 2.52 Å. The Cl(3)O₄ anion forms hydrogen bonds with four dications, resulting in the creation of a 2D sheet, as in [2]. One perchlorate oxygen atom O(3) is a treble acceptor and interacts with H(8), H(14), and H(33) attached to C(8), C(14), and C(33) with hydrogen bond lengths of 2.54 Å, 2.48 Å and 2.42 Å. The second perchlorate oxygen atom O(4) is a double acceptor and interacts with H(7) and H(30) attached to C(7) and C(30) with hydrogen bond lengths of 2.34 Å and 2.57 Å. The third perchlorate oxygen atom O(1) interacts with H(31) attached to C(31) with a hydrogen bond length of 2.27 Å.

CONCLUSIONS

We have successfully synthesized two substituted 4'-phenyl terpyridine Fe compounds: [Fe(3-NO₂phtpy)₂](ClO₄)₂ and [Fe(3-Clphtpy)₂](ClO₄)₂. Their structures have been determined by the X-ray diffraction analysis and discussed. They show a new type of the crystal packing mode for [M(4'-Phtpy)₂]²⁺ compounds.

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