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Synthesis and Crystal Structure of Metal Complexes Based on 2,6-*bis*(6-Methylquinolin-2-yl)pyridine Ligand[1]

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Abstract—Two mononuclear five-coordinated transition metal complexes $FeLCl_2$ (**I**) and $MnLCl_2$ (**II**) containing tridentate 2,6-*bis*(6-methylquinolin-2-yl)pyridine ligand (L) have been synthesized and characterized by single-crystal X-ray crystallography. In the complexes, the metal center was tridentately chelated by ligand and further coordinated by two chlorine atoms, resulting in distorted trigonal-bipyramidal geometry for complex **I** and **II**, respectively. In addition, crystal packing in complex is stabilized by C—H···Cl intermolecular hydrogen bond, which link the mononuclear complex to the 1D chain.

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INTRODUCTION

Hydro(solvo)thermal syntheses carried out in superheated solvent systems provides ideal conditions for the crystal growth owing to the enhanced transport ability of the solvents [1–6]. Besides, recent studies revealed that crystal growth under hydro(solvo)thermal conditions occasionally involves in situ ligand synthesis which not only provides a powerful synthesis method for organic ligands which are difficult to synthesize but also represents a potential new direction for novel inorganic-organic hybrid network construction through crystal engineering [7]. In the present paper, we report the syntheses and crystal structures of two novel transition metal complexes bearing tridentate 2,6-*bis*(6-methylquinolin-2-yl)pyridine ligand (**L**) under solvothermal conditions. During the course of the solvothermal treatment, new carbon—carbon bond would format through reductive coupling or oxidative coupling [8, 9]. Herein, ethanol and ligand 2,6-*bis*(*p*-tolylimino)pyridine ($\mathbf{L^1}$) produced the new carbon—carbon bond connecting imino group and benzene to form a hexatomic ring and new ligand 2,6-*bis*(6-methylquinolin-2-yl)pyridine L was obtained. Consequently, treatment of the chelate schiff-base ligand L^1 with $FeCl_2$ or $MnCl_2$ yielded the corresponding metal complexes **I** and **II**. These complexes were characterized by X-ray single crystal diffraction. The Fe atom and Mn atom in the complexes are five-coordinated by one pyridine atom and two N atoms of the quinoline group, and two chlorine atoms, forming distorted trigonal-biyramid geometry.

EXPERIMENTAL

2,6-Pyridinedicarboxaldehyde was prepared by oxidation of 2,6-pyridinemethanol with activated MnO_2 according to the procedure described in the literature [10]. All reagents used in the syntheses were of analytical grade and used without further purification as received. Elemental analyses for carbon, hydrogen and nitrogen were performed on a VarioEL III elemental analyzer. ^1H NMR data were collected from INOVA-400 MHz NMR system. The infrared spectra (4000–400 cm^{-1}) were recorded by using KBr pellet on a BRUKER EQUINOX-55 IR spectrometer.

Synthesis of the ligand $\mathbf{L^1}$. *p*-Toluidime (0.5397 g, 5.0 mmol) dissolved in ethanol (10 mL) was added to a solution of 2,6-pyridine dicarboxaldehyde (0.3313 g, 2.5 mmol) in ethanol (6.0 mL). The solution was refluxed for 3 h after addition of several drops glacial acetic acid. Then the solution was cooled to room temperature and filtered. Residue was washed with hexane. The product was crystallized from ethanol by recrystallization. Finally, the light yellow needle-like particles were dried in vacuo. The yield was 69.7%, m.p. 178.8–179.3°C. ^1H NMR (400 MHz; $CDCl_3$; δ, ppm): 8.44 (d., $J = 7.3$ Hz, 2H), 8.19 (t., $J = 7.6$ Hz,

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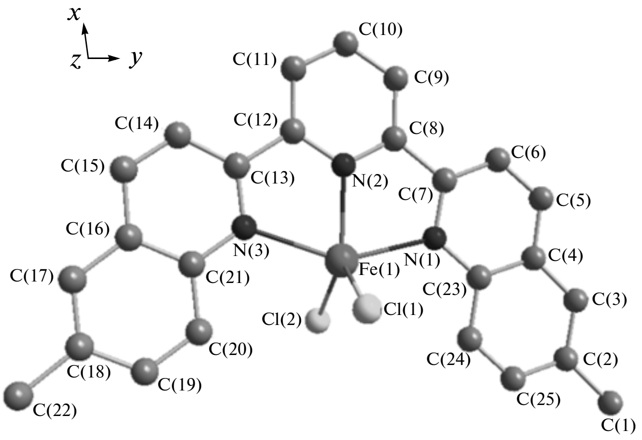

Fig. 1. The crystal structure of complex **I**.

1H), 7.75 (s., 2H), 7.55 (d., $J = 8.4$ Hz, 8H), 3.71 (s., 1H), 2.42 (s., 6H).

For $C_{21}H_{19}N_3$

anal. calcd., %:	C, 80.48;	H, 6.110;	N, 13.41.
Found, %:	C, 79.62;	H, 6.094;	N, 13.34.

IR spectrum (KBr; ν, cm^{-1}): 3168, 1612, 1471, 1429, 1268, 962, 815, 763.

Synthesis of I. 2,6-*Bis*(*p*-tolylimino)pyridine (0.0160 g, 0.05 mmol) and $FeCl_2 \cdot 4H_2O$ (0.0197 g, 0.05 mmol) along with four drops of 0.1 M hydrochloric acid were dissolved in ethanol (10 mL). The mixture was heated in a Teflon-lined, stainless-steel Parr bomb at 373 K for 120 h. The bomb was cooled at 5 K per hour. Deep red crystals were obtained.

For $C_{25}H_{19}N_3Cl_2Fe$

anal. calcd., %:	C, 61.51;	H, 3.92;	N, 8.61.
Found, %:	C, 62.03;	H, 3.556;	N, 8.392.

IR spectrum (KBr; ν, cm^{-1}): 3172, 1602, 1471, 1409, 1268, 968, 819, 763, 592.

Synthesis of II. 2,6-*Bis*(*p*-tolylimino)pyridine (0.0160 g, 0.05 mmol), and $MnCl_2 \cdot 4H_2O$ (0.0143 g, 0.05 mmol) along with five drops of 0.1 M hydrochloric acid were dissolved in ethanol (10 mL). The mixture was heated in a Teflon-lined, stainless-steel Parr bomb at 373 K for 120 h. The bomb was cooled at 5 K per hour. Orange red crystals were obtained.

For $C_{25}H_{19}N_3Cl_2Mn$

anal. calcd., %:	C, 61.62;	H, 3.93;	N, 8.62.
Found, %:	C, 61.83;	H, 4.186;	N, 8.986.

IR spectrum (KBr; ν, cm^{-1}): 3214, 1600, 1471, 1415, 1376, 998, 815, 763, 630.

X-ray crystallography. Single crystal of the complex **I** and **II** were put on a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) by using a ϕ/ω scan technique at room temperature. The structure was solved by direct methods with SHELXS-97 [11]. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restrains, while the non-hydrogen atoms were treated with common anisotropic displacement factors and included in the final refinement with geometrical restrains. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 [12]. The final agreement factor values for complex **I** are $R = 0.0413$ and $wR = 0.1095$; for complex **II** are $R = 0.0710$ and $wR = 0.1468$. Crystallographic data and refinement parameters are listed in Table 1. The atomic coordinates and other parameters of the complexes have been deposited with the Cambridge Crystallographic Data Centre (nos. 783341 (**I**) and 830837 (**II**); deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

X-ray single crystal diffraction analysis reveals that complexes **I** and **II** almost have the same coordination geometry. Therefore, we just describe complex **I** as follow. The crystal structure of complex **I** is shown in Fig. 1, and selected bond distances and angles were given in Table 2. Complex **I** displays an approximate C_2 symmetry about a plane containing the iron atom, the two chlorine atoms, and the pyridyl nitrogen atom [13]. The central pyridine ring, iron ion and two quinoline groups are approximate in the same plane. The iron ion is in the center by 0.046 Å deviate from this coordinated plane. And the Fe atom, two chlorine atoms and pyridyl nitrogen atom are in the same plane,

Table 1. Crystal data and structure refinement information for compounds **I** and **II**

Parameter	Value	
	I	**II**
Formular weight	488.18	487.27
Crystal system	Triclinic	Triclinic
Crystal size, mm	0.28 × 0.19 × 0.09	0.31 × 0.25 × 0.14
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	9.6702(13)	9.7165(12)
b, Å	10.3085(14)	10.4342(14)
c, Å	11.0076(14)	10.8126(14)
α, deg	95.055(2)	95.572(2)
β, deg	95.535(2)	97.714(2)
λ, deg	95.806(2)	95.310(2)
Z; volume, Å^3	2; 1081.3(2)	2; 1075.0(2)
ρ_{calcd}, g/cm^3	1.499	1.505
$\mu(MoK_\alpha)$, mm^{-1}	0.963	0.881
$F(000)$	500	498
θ Range, deg	1.87–25.10	1.91–25.09
Limiting indices h, k, l	$-11 < h < 9, -12 < k < 12, -13 < l < 10$	$-11 < h < 11, -12 < k < 12, -12 < l < 10$
Reflections collected	5479	5467
Reflections with $I > 2\sigma(I)$	2877	2955
Independent reflections (R_{int})	3787(0.0184)	3783(0.0238)
Data/restraints/parameters	3787/0/282	3783/0/282
Goodness-of-fit on F^2	1.080	1.094
Final R indices ($I > 2\sigma(I)$)	$R = 0.0413$, $wR = 0.1095$	$R = 0.0710$, $wR = 0.1468$
R indices (all data)	$R = 0.0582$, $wR = 0.1302$	$R = 0.0912$, $wR = 0.1578$
$\Delta\rho_{min}/\Delta\rho_{max}$, e Å^{-3}	–0.221/0.336	–0.528/0.919

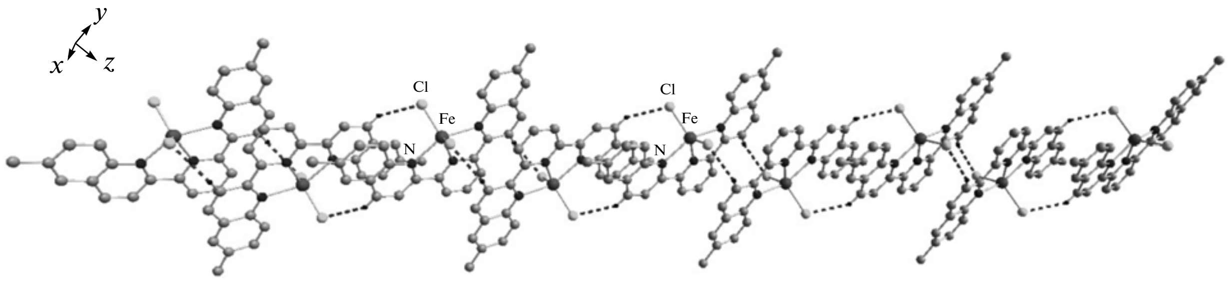

Fig. 2. 1D chain coordination motif of complex **I**.

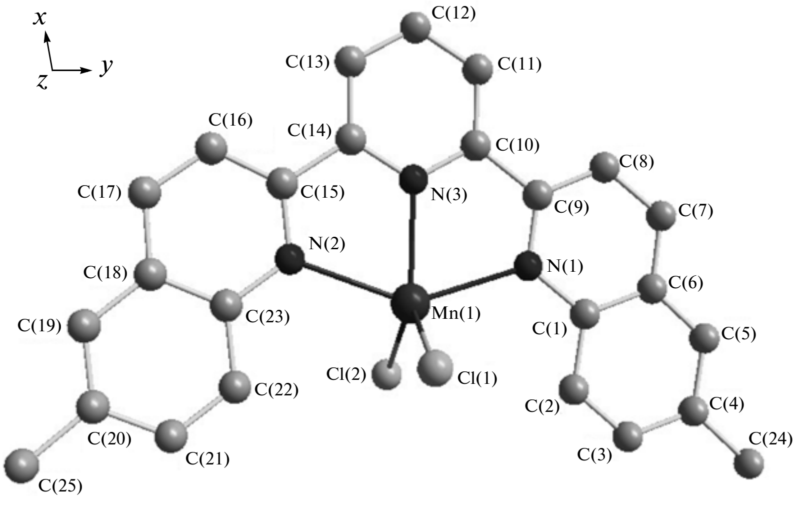

Fig. 3. The crystal structure of complex **II**.

the dihedral angle between the ligand plane (N(1), N(2), N(3)) and the equatorial plane (Cl(1), Cl(2), N(3)) is 89.78(2)°. The coordination geometry of the central iron ion can be described as distorted trigonal-bipyramidal, with the two chlorine atoms and the pyridyl nitrogen atom forming the equatorial plane [14]. The bond length of Fe(1)–Cl(2) (2.3488(11) Å) is longer than that of Fe(1)–Cl(1) (2.2793(11) Å), which can be ascribed to apical elongation in the square-pyramidal complex. The equatorial angles range in

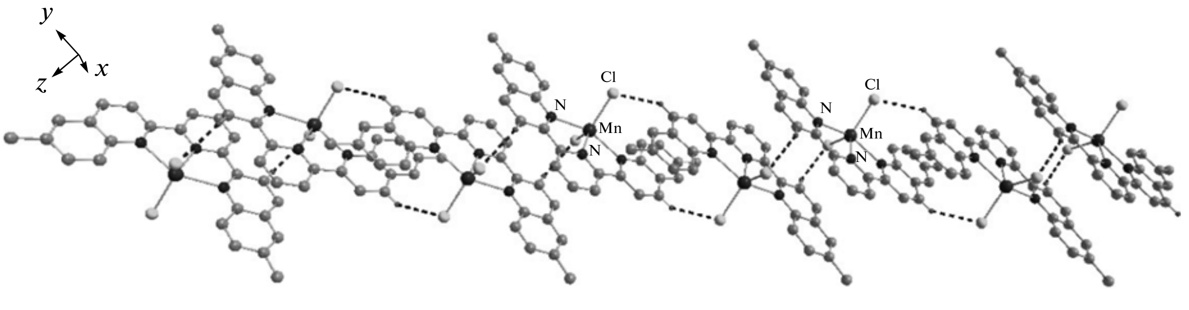

Fig. 4. 1D chain coordination motif of complex **II**.

118.22(4)°–121.492(80)°, and the two axial Fe–N bonds subtend an angle of 148.567(79)°. Intermolecular hydrogen bonds are also found in the crystal of **I**. Figure 2 shows the molecular arrangement of **I**. The C–H group in the benzene ring plays a key role. The intermolecular hydrogen bonds occur between C–H and coordinated chlorine atom (2.7760 Å for C–H···Cl). Thus the units of $FeLCl_2$ were connected as 1D chain structure by the intermolecular hydrogen bonds [15]. In addition, the crystal structure and 1D chain structure of complex **II** are shown in Figs. 3 and 4, respectively.

Table 2. The selected bond lengths (Å) and bond angles (deg) for **I** and **II**

I		**II**	
Bond	d, Å	Bond	d, Å
Fe(1)–N(1)	2.255(3)	Mn(1)–N(1)	2.339(4)
Fe(1)–N(2)	2.100(3)	Mn(1)–N(3)	2.192(4)
Fe(1)–N(3)	2.246(3)	Mn(1)–N(2)	2.312(4)
Fe(1)–Cl(1)	2.2793(12)	Mn(1)–Cl(1)	2.3319(18)
Fe(1)–Cl(2)	2.3488(10)	Mn(1)–Cl(2)	2.3747(17)
N(1)–C(7)	1.335(4)	N(1)–C(9)	1.301(6)
N(1)–C(23)	1.370(4)	N(1)–C(1)	1.401(6)
N(2)–C(12)	1.342(4)	N(2)–C(15)	1.319(6)
N(2)–C(8)	1.351(4)	N(2)–C(23)	1.382(6)
N(3)–C(13)	1.324(4)	N(3)–C(14)	1.340(6)
N(3)–C(21)	1.376(4)	N(3)–C(10)	1.343(6)
C(1)–C(2)	1.510(5)	C(1)–C(2)	1.392(7)
Angle	ω, deg	Angle	ω, deg
N(2)Fe(1)N(3)	74.33(10)	N(3)Mn(1)N(2)	72.42(14)
N(2)Fe(1)N(1)	74.37(10)	N(3)Mn(1)Cl(1)	118.53(12)
N(3)Fe(1)N(1)	148.57(10)	N(2)Mn(1)Cl(1)	99.22(11)
N(2)Fe(1)Cl(1)	120.27(8)	N(3)Mn(1)N(1)	71.63(14)
N(3)Fe(1)Cl(1)	99.55(7)	N(2)Mn(1)N(1)	144.01(14)
N(1)Fe(1)Cl(1)	98.51(8)	N(1)Mn(1)Cl(2)	99.64(11)
N(2)Fe(1)Cl(2)	121.51(8)	N(3)Mn(1)Cl(2)	123.26(12)
N(3)Fe(1)Cl(2)	96.55(7)	N(2)Mn(1)Cl(2)	98.28(11)
N(1)Fe(1)Cl(2)	97.28(7)	Cl(1)Mn(1)Cl(2)	118.21(7)
Cl(1)Fe(1)Cl(2)	118.22(5)	Cl(1)Mn(1)N(1)	99.37(11)
C(7)N(1)C(23)	118.4(3)	C(9)N(1)C(1)	119.9(4)
C(7)N(1)Fe(1)	114.5(2)	C(9)N(1)Mn(1)	114.8(3)
C(23)N(1)Fe(1)	127.0(2)	C(1)N(1)Mn(1)	125.2(3)
C(7)N(1)Fe(1)	114.5(2)	C(15)N(2)Mn(1)	115.3(3)
C(12)N(2)Fe(1)	119.9(2)	C(23)N(2)Mn(1)	125.1(3)
C(8)N(2)Fe(1)	120.3(2)	C(14)N(3)Mn(1)	119.4(3)
C(13)N(3)Fe(1)	114.7(2)	C(10)N(3)Mn(1)	120.3(3)

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