Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2020, **30**, 100–102

Mendeleev Communications

Synthesis and structures of two mononuclear iron(II) complexes derived from polypyridine ligands

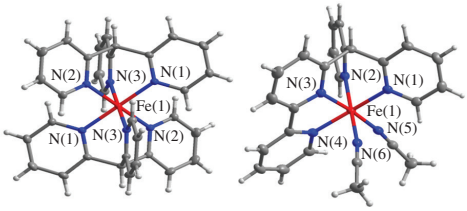
Hongqiao Wang,[a,b] Nan Wu,[a] Jing Zheng,[a] Chunyang Zheng*[a,b] and Dunjia Wang[a]

[a] *Hubei Key Laboratory of Pollutant Analysis and Reuse Technology, Hubei Normal University, Huangshi 435002, P. R. China. E-mail: zcy800204@163.com*

[b] *Department of Chemistry, The School of Art and Science of Hubei Normal University, Huangshi 435002, P. R. China*

DOI: 10.1016/j.mencom.2020.01.033

Three polypyridine ligands such as tri(2-pyridyl)methane, (2,2′-bipyridin-6-yl)di(2-pyridyl)methane and 2,6-bis[di(2-pyridyl)methyl]pyridine as well as their new iron(II) mononuclear complexes have been obtained in a one-pot synthesis. Detailed structural analyses and magnetic susceptibility measurements confirm the expected six-coordinate octahedral geometry and the metric parameters are consistent with low-spin iron(II) in the complexes.



low-spin

Keywords: polypyridine, one-pot synthesis, metal complexes, low-spin.

Polypyridine compounds are excellent ligands for building up large polymetallic compounds as they stabilize a single labile coordination site in transition metal coordination compounds. They attract considerable attention due to their fascinating photo- and electrochemistry properties.[1,2] The majority of ligands have N(2), N(3), N(4) or N(5) donor sets, therefore their electronic properties may be tuned by varying the combination of N donors as well as substituents (electron-withdrawing *vs.* electron-donating).[3–5] Of considerable interest are their applications in metallo-supramolecular chemistry and their presence in coordination compounds possessing interesting magnetic properties which can be rationally designed, predictably assembled and easily modified.[1,2]

Among numerous polypyridine ligands, tri(2-pyridyl)methane (Py_3) and its derivatives have been synthesized and their transition metal coordination compounds have been studied in terms of tripodal acceptor ligands.[6,7] In the recent year, we have studied some new cyano-bridged heterometallic molecular clusters with reversible charge-transfer-induced spin transition (CTIST) or spin crossover (SCO) behavior.[8,9] We have reported two iron(II) tri(pyridyl)phosphine sulfide compounds lacking spin crossover behavior.[10] In order to design and produce SCO systems that can be tuned at room temperature, we have synthesized some polypyridine ligands to adjust the ligand-field strength on the Fe^{II} centres. Herein, we report on the syntheses of tripodal tri(2-pyridyl)methane (Py_3), new tetradendate (2,2′-bipyridin-6-yl)di(2-pyridyl)methane (Py_4), and pentadendate 2,6-bis[di(2-pyridyl)methyl]pyridine (Py_5). Crystal structure study of two new iron(II) mononuclear coordination compounds, *viz.* $[Fe(Py_3)_2][ClO_4]_2{\cdot}2DMF$ **1** and $[Fe(Py_4)(MeCN)_2][ClO_4]_2{\cdot}H_2O$ **2**, was also performed.

Ligands Py_3, Py_4 and Py_5 were obtained by one-pot procedures (Scheme 1). Di(2-pyridyl)methane was prepared *in situ* by treatment of lithiated 2-methylpyridine (LiC_6H_6N) with 0.5 equiv. of 2-fluoropyridine, which allowed us to avoid formation of side products.[11,12] The role of the second equivalent of LiC_6H_6N was to cause deprotonation in initially formed di(2-pyridyl)methane leading finally to carbaninon **A**. Treatment of this carbanion with the appropriate electrophiles enabled performing the next stage in the same vessel (see Scheme 1, steps iv, vi, vii) to afford ligands Py_4, Py_3 and Py_5.[†] The crystal structure of Py_5 was confirmed by X-ray crystallography (Figure 1).[‡]

The synthesis of two metal coordination compounds **1** and **2** was carried out by reaction of 2 equiv. of Py_3 and 1 equiv. of Py_4 with $Fe(ClO_4)_2{\cdot}6H_2O$ salt in DMF or MeCN under an N_2 atmosphere.[§] Interestingly, variation in reactant ratio [Py_4/$Fe(ClO_4)_2{\cdot}6H_2O$ being 1 : 1, 2 : 1 or 2 : 1] resulted in the same complex **2**.

The molecular structures of compounds **1** and **2** were determined by X-ray crystallography at 296 K and 100 K, respectively (see Figure 1).[‡] Complexes **1** and **2** crystallize in the monoclinic space

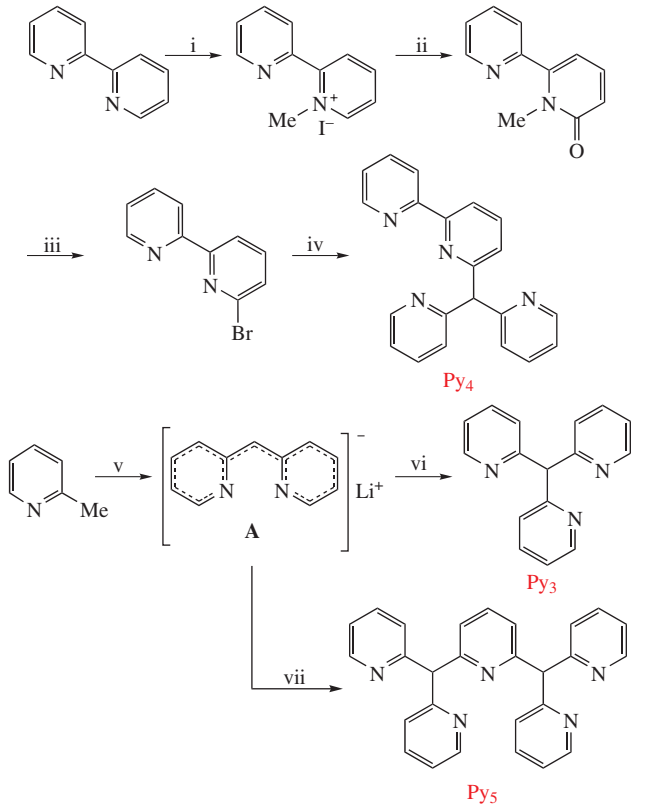
[†] *(2,2′-Bipyridin-6-yl)di(2-pyridyl)methane* (Py_4). ^{1}H NMR (300 MHz, $CDC1_3$) δ: 8.59–8.65 (m, 3H), 8.26–8.30 (m, 2H), 7.62–7.80 (m, 5H), 7.36–7.40 (m, 3H), 7.15–7.19 (m, 2H), 6.12 (s, 1H). MS (ESI), *m/z*: 325.22 ($[M+H]^+$), 671.00 ($[2M+Na]^+$).

Tri(2-pyridyl)methane (Py_3). ^{1}H NMR (300 MHz, $CDC1_3$) δ: 8.57–8.60 (m, 3H), 7.59–7.65 (m, 3H), 7.33 (d, 3H), 7.15 (t, 3H), 6.00 (s, 1H). MS (ESI), *m/z*: 248.15 ($[M+H]^+$), 516.93 ($[2M+Na]^+$).

2,6-Bis[di(2-pyridyl)methyl]pyridine (Py_5). ^{1}H NMR (300 MHz, $CDC1_3$) δ: 8.53 (dd, 4H, *J* 4.8 Hz, *J* 0.8 Hz), 7.47–7.61 (m, 5H), 7.17–7.21 (m, 6H), 7.07–7.12 (m, 4H), 5.93 (s, 2H). MS (ESI), *m/z*: 416.33 ($[M+H]^+$), 438.18 ($[M+Na]^+$).

[‡] *Crystal data for* (Py_5). $C_{27}H_{21}N_5$, M = 415.49, monoclinic, space group C_2, a = 16.031(3), b = 7.3086(15) and c = 12.132(4) Å, β = 130.676(2)°, V = 1078.0(5) Å^3, Z = 2, d_{calc} = 1.280 g cm^{-3}, μ(MoKα) = 0.078 mm^{-1}, T = 296(2) K, 7119 reflections measured, 3084 independent reflections (R_{int} = 0.0454), final R_1 = 0.0500 [$I > 2\sigma(I)$], wR_2 = 0.1361, GOF = 1.086.

Crystal data for **1**. $C_{38}H_{40}C_{12}FeN_8O_{10}$, M = 895.53, monoclinic, space group $P2_1/n$, a = 12.4008(6), b = 12.8255(6) and c = 13.8889(7) Å, β = 112.111(2)°, V = 2046.52(17) Å^3, Z = 2, d_{calc} = 1.453 g cm^{-3}, μ(MoKα) = 0.566 mm^{-1}, T = 296(2) K, 22473 reflections measured, 6488 independent reflections (R_{int} = 0.0496), final R_1 = 0.0599 [$I > 2\sigma(I)$], wR_2 = 0.1516, GOF = 1.030.



Scheme 1 *Reagents and conditions*: i, MeI; ii, $K_3Fe(CN)_6$; iii, Br_2, PPh_3; iv, BuLi, THF, –78 °C, then 2-fluoropyridine, –20 °C, then reflux, 1 h; v, LiC_6H_6N; vi, 2-fluoropyridine; vii, 2,6-difluoropyridine.

group $P2_1/n$ and triclinic space group $P\bar{1}$ with two DMF molecules in **1** and one H_2O molecules in **2**, respectively. Ligand Py_3 acts as tripodal one and the Fe^{II} atom lies on an inversion center and is octahedrally coordinated by all the N atoms with expected six-coordinate geometry. In complex **2**, Fe^{II} ion is surrounded by six nitrogen atoms from one Py_4 ligand and two MeCN molecules.

The coordination Fe–N bond lengths (Table 1) in complex **1** (average 1.980 Å) and **2** (average 1.9532 Å) are similar to reported average $[Fe–N(py)_6]^{2+}$ bond length in $[FeL_2]^{2+}$ based on 1,1,1-tri-(2-pyridyl)ethane ligand.[13] In addition, the distortion parameter values Σ of geometries around Fe^{II} ions are 14.4° for **1** and 48.5° for **2**, respectively. Moreover, the Fe(1)–N(3) bond length (1.904 Å) in complex **2** is obviously shorter than other Fe(1)–N(3) bond lengths (from 1.941 to 1.986 Å), and the value Σ (48.5°) in complex **2** is

Crystal data for **2**. $C_{25}H_{24}C_{12}FeN_6O_9$, M = 679.25, triclinic, space group $P\bar{1}$, a = 10.9963(11), b = 11.8255(10) and c = 12.1227(12) Å, α = 77.3000(10)°, β = 64.4770(10)°, γ = 82.6570(10)°, V = 1386.8(2) Å^3, Z = 2, d_{calc} = = 1.627 cm^{-3}, μ(MoKα) = 0.802 mm^{-1}, T = 100(2) K, 9766 reflections measured, 5278 independent reflections (R_{int} = 0.0356), final R_1 = 0.0406 [$I > 2\sigma(I)$], wR_2 = 0.0925, GOF = 1.029.

CCDC 1935066, 1578633 and 1578634 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

§ *Synthesis of* $[Fe(Py_3)_2][ClO_4]_2 \cdot 2HC(O)NMe_2$ **1**. A solution of $Fe(ClO_4)_2 \cdot 6H_2O$ (0.036 g, 0.1 mmol) and Py_3 (0.052 mg, 0.2 mmol) in DMF (3 ml) was stirred at room temperature for 2 h under an argon atmosphere. Then it was placed under the diffusion of diethyl ether vapor slowly without disturbance. Dark-red blocks crystals suitable for X-ray structure analysis were grown within about 7 days. Yield 0.060 g.

Synthesis of $[Fe(Py_4)(MeCN)_2][ClO_4]_2 \cdot H_2O$ **2**. A solution of $Fe(ClO_4)_2 \cdot 6H_2O$ (0.036 g, 0.1 mmol) and Py_4 (0.032 mg, 0.1 mmol) in MeCN (3 ml) was stirred at room temperature for 2 h under an argon atmosphere. Then it was placed under the slow diffusion of diethyl ether vapor without disturbance. Dark-red blocks crystals suitable for X-ray structure analysis were obtained within about 8 days. Yield 0.032 g.

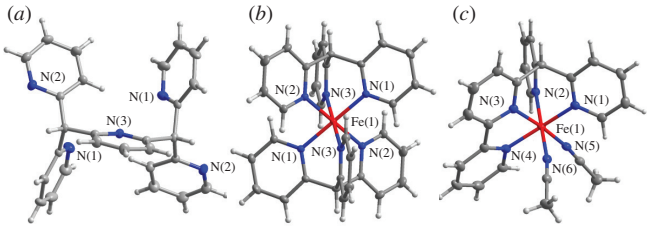


Figure 1 Molecular structures of (*a*) Py_5 , (*b*) complex **1** and (*c*) complex **2**; anions and solvent molecules are omitted for clarity.

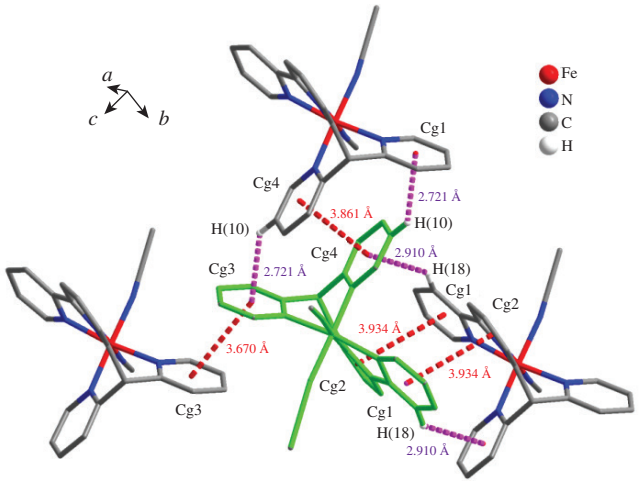


Figure 2 Packing diagram of molecules **1** illustrating intermolecular C–H···π and π–π interactions; anions, solvent molecules and part of hydrogen atoms are omitted for clarity. Symbols Cg1, Cg2, Cg3 and Cg4 denote the centroids of four pyridine rings [N(4),C(17)–C(21)], [N(3),C(12)–C(16)], [N(1),C(1)–C(5)] and [N(2),C(7)–C(11)], respectively.

larger than that (14.4°) in **1**. The above mentioned phenomenon may be caused by the steric hindrance effect of the ligand Py_4. In general, high spin Fe^{II} ions tend to form more distorted octahedra and thus have larger Σ value than their low spin counterparts.[14] According to above structural analysis, we can infer that the spin state of Fe^{II} ion in **1** and **2** is the LS state. The $\chi_M T$ values (see Figure S1, Online Supplementary Materials) of **1** and **2** are below 0.1 cm^3 K mol^{-1} at 250 K and agree with the expected value for LS Fe^{II} unit, which is also confirmed by the above crystallographic data and is in agreement with a low-spin iron(II) in N(6) surrounding. In complex **2**, short intermolecular π–π interactions are found between the coordinated pyridine ligands and the pyridine ligands (3.861, 3.934 and 3.670 Å). In addition, in the crystal structure of **2** there are weak C–H···π intermolecular hydrogen bonds (2.721 and 2.910 Å), and the stability of the crystal structure can be accounted by these interactions (Figure 2).

In summary, a tripodal ligand tri(2-pyridyl)methane (Py_3) and new tetradendate ligand (2,2′-bipyridin-6-yl)di(2-pyridyl)methane (Py_4) have been synthesized by a high-yielding one-pot procedure

Table 1 Mean Fe^{II}–N bond lengths (Å) and distortion parameters (°) for complexes **1** and **2**.

	Complex **1**	Complex **2**
Fe(1)–N(1)	1.9795(14)	1.9858(15)
Fe(1)–N(2)	1.9783(14)	1.9563(15)
Fe(1)–N(3)	1.9821(14)	1.9036(15)
Fe(1)–N(4)		1.9861(15)
Fe(1)–N(5)		1.9410(15)
Fe(1)–N(6)		1.9470(16)
Fe(1)–N(average)	1.9800(14)	1.9533(15)
$\Sigma_{Fe(1)}$[a]	14.4	48.5

[a] The sum of the deviation from 90° of the 12 *cis*-angles of the FeN_6 octahedron.

using inexpensive substrates. Based on these two polypyridine ligands, two mononuclear iron(II) complexes have been obtained. The expected six-coordinate octahedral geometry has been confirmed by structural analyses and magnetic susceptibility measurements, and the metric parameters are consistent with low-spin iron(II) in **1** and **2**. The structural analysis of complex **2** has revealed that the $[Fe(Py_4)]^{2+}$ entity possesses two accessible coordination sites, which indicates that the mononuclear iron(II) complex can be obtained using the co-ligand NCX^- (X = S, Se, or BH_3). Further studies on the fabrication of new iron(II) metal coordination compounds with the new Py_4 ligand showing SCO behavior are ongoing.

This work was supported by the Science and Technology Foundation for Creative Research Group of HBDE (T201810), the National Undergraduate Training Program for Innovation and Entrepreneurship (project no. 201813256003) and the Key Fund of The School of Art and Science of Hubei Normal University (project no. Ky201701).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.01.033.

References

1 A. Cannizzo, C. J. Milne, C. Consani, W. Gawelda, C. Bressler, F. van Mourik and M. Chergui, *Coord. Chem. Rev.*, 2010, **254**, 2677.
2 M. Nippe, R. S. Khnayzer, J. A. Panetier, D. Z. Zee, B. S. Olaiya, M. Head-Gordon, C. J. Chang, F. N. Castellano and J. R. Long, *Chem. Sci.*, 2013, **4**, 3934.
3 B. A. Trofimov, N. K. Gusarova, A. V. Artem'ev, S. F. Malysheva, N. A. Belogorlova, A. O. Korocheva, O. N. Kazheva, G. G. Alexandrov and O. A. Dyachenko, *Mendeleev Commun.*, 2012, **22**, 187.
4 A. V. Artem'ev, N. K. Gusarova, S. F. Malysheva, N. A. Belogorlova, O. N. Kazheva, G. G. Alexandrov, O. A. Dyachenko and B. A. Trofimov, *Mendeleev Commun.*, 2015, **25**, 196.
5 A. V. Kharcheva, D. A. Evdokimov, M. D. Reshetova, V. I. Yuzhakov, S. V. Patsaeva and N. E. Borisova, *Mendeleev Commun.*, 2017, **27**, 459.
6 H.-M. Berends, A.-M. Manke, C. Näther, F. Tuczek and P. Kurz, *Dalton Trans.*, 2012, **41**, 6215.
7 D. Wiedemann and A. Grohmann, *Dalton Trans.*, 2014, **43**, 2406.
8 C. Zheng, J. Xu, Z. Yang, J. Tao and D. Li, *Inorg. Chem.*, 2015, **54**, 9687.
9 C. Zheng, J. Xu, F. Wang, J. Tao and D. Li, *Dalton Trans.*, 2016, **45**, 17254.
10 C. Zheng, X. Hu and Q. Tao, *Mendeleev Commun.*, 2018, **28**, 28.
11 G. Dyker and O. Muth, *Eur. J. Org. Chem.*, 2004, 4319.
12 E. A. Ünal, D. Wiedemann, J. Seiffert, J. P. Boyd and A. Grohmann, *Tetrahedron Lett.*, 2012, **53**, 54.
13 A. Santoro, C. Sambiagio, P. C. McGowan and M. A. Halcrow, *Dalton Trans.*, 2015, **44**, 1060.
14 M. A. Halcrow, *Chem. Soc. Rev.*, 2011, **40**, 4119.

Received: 24th June 2019; Com. 19/5963