Inorganic Chemistry Communications 19 (2012) 4–9

Contents lists available at SciVerse ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

# V-shaped $Fe_3^{III}$ and linear $Fe^{II}/Fe^{III}/Fe^{II}$ complexes supported by phenyl-pyridine-2-yl-methanone oxime ligand: Solvothermal syntheses, structures and magnetic property

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ARTICLE INFO

*Article history:*
Received 19 December 2011
Accepted 20 January 2012
Available online 28 January 2012

*Keywords:*
Crystal structures
Multinuclear iron complexes
Solvothermal synthesis
*In situ* reaction
Magnetic properties

ABSTRACT

Under solvothermal conditions, one polynuclear $Fe^{III}$ complex of formula $[Fe_3\{(py)C(ph)O\}_4Cl_4][FeCl_4]$ (**1**) was synthesized from reaction of phenyl-pyridine-2-yl-methanone oxime (py)C(ph)NOH with $FeCl_3$, and one $Fe^{II}/Fe^{III}/Fe^{II}$ complex of composition $[Fe_3\{(py)C(ph)NO\}_6][CH_3COO]$ (**2**) was prepared from treatment of (py)C(ph)NOH with $Fe(OAc)_2$. The most interesting synthetic feature of complex **1** is the *in situ* transformation of (py)C(ph)NOH into the $(py)C(ph)O^-$ ligand. Complexes **1** and **2** were characterized by X-ray single crystal diffraction, IR spectroscopy, and elemental analysis. X-ray analysis revealed that complex **1** contains a V-shaped $Fe^{III}$ core with two terminal $Fe^{III}$ atoms displaying distorted square-pyramidal geometries and one central $Fe^{III}$ ion exhibiting octahedron geometry. Complex **2** is a mixed-valence linear $Fe^{II}/Fe^{III}/Fe^{II}$ complex with all the three metal centers displaying distorted octahedron geometries. The low-temperature magnetic susceptibility measurement for the solid sample of **1** revealed the weak antiferromagnetic $Fe^{III}\cdots Fe^{III}$ interactions. Theoretical calculations based on density functional theory were performed using the crystal structure of complex **1**.

Design and investigation of high-nuclearity paramagnetic transition metal complexes with oxygen- and/or nitrogen based ligation continue to attract intense attention [1], due to their potential applications as functional materials, *e.g.*, magnetic [2], optical [3], electronic [4] and catalytic [5] etc., and their relevance to enzyme active centers in biological systems [6]. The synthetic strategies for constructing these complexes involve the continuous development of new synthetic methods, the dexterous introduction of ancillary ligands, and the rational selection of appropriate metal salts as the starting materials. Solvothermal technique has been proved as an effective synthetic method since past decade, because solvothermal technique allows the application of high temperatures to reactions in low or relatively low boiling solvents and could directly generate pure, crystalline polynuclear products in good yields. *In situ* metal/ligand reactions under solvothermal conditions occur occasionally, which may result in the generation of novel coordination compounds exhibiting structural diversity and unique properties [7]. The organic oximate compounds are fertile ligands for the preparation of 3d-metal clusters, since the oximate compounds possess the bridging groups that can foster formation of polynuclear products. A plenty of coordination compounds supported by the oximate ligands with aesthetically pleasing structures and versatile magnetic properties have been prepared [8].

We have been interested in synthesizing polynuclear complexes by combining the above mentioned strategies. In the present work, we have used (py)C(ph)NOH in combination with solvothermal method for the synthesis of new multinuclear iron complexes. The use of the anionic ligand $(py)C(ph)NO^-$ had previously given a plethora of $Mn^{II}Mn^{III}$ [9], $Mn^{II}Mn^{IV}$ [10], $Co^{II}Co^{III}$ [11], $Cu^{II}$ [12], $Ni^{II}$ [13] and $Zn^{II}$ [14] polynuclear compounds, but they were all synthesized by "conventional" coordination chemistry techniques, *i.e.*, solution chemistry under atmospheric pressure and at temperatures limited to the boiling points of common solvents. The coordination chemistry of $(py)C(ph)NO^-$ with $Fe^{II}$ and $Fe^{III}$ has been little explored, with only a $Fe_2^{III}$ complex [15] having been prepared by the conventional coordination chemistry techniques. We assume that there might be a number of other high-nuclearity $Fe^{II}$ or $Fe^{III}/(py)C(ph)NO^-$ species available by adopting solvothermal method, and we have now discovered a route to the polynuclear $[Fe_3\{(py)C(ph)O\}_4Cl_4][FeCl_4]$ (**1**) and $[Fe_3\{(py)C(ph)NO\}_6][CH_3COO]$ (**2**) complexes. Herein, we report the syntheses, structural characterizations of **1** and **2**. The magnetic study of **1** was also presented.

Complexes **1** and **2** were prepared under solvothermal conditions in EtOH. Treatment of $FeCl_3$ with (py)C(ph)NOH in EtOH results in

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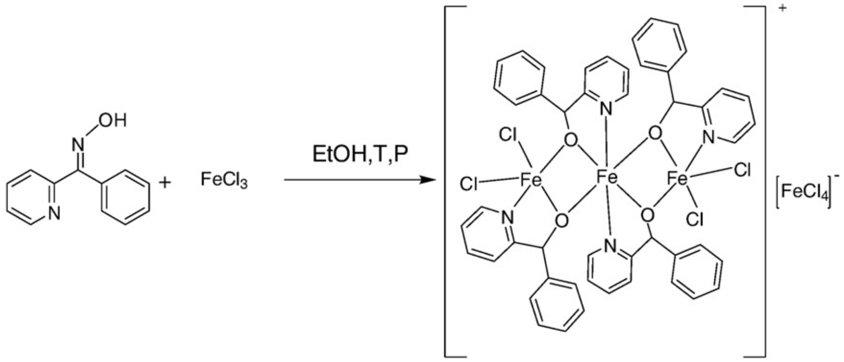
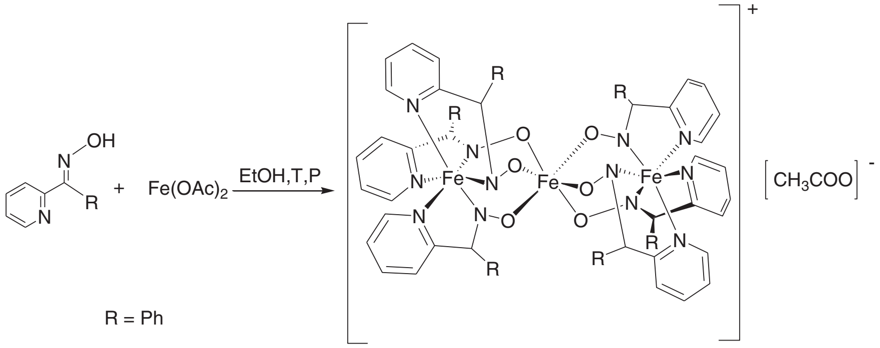
doi:10.1016/j.inoche.2012.01.015



**Scheme 1.** Synthesis of complex **1.**



**Scheme 2.** Synthesis of complex **2.**

the formation of **1** (Scheme 1). The most remarkable feature of this reaction is the *in situ* formation of the (py)C(ph)O$^-$ ligand. The mechanism of the *in situ* formation of the (py)C(ph)O$^-$ ligand is unknown now. It is proposed that the first step of this transformation involves the hydrolysis of (py)C(ph)NOH to phenyl(pyridin-2-yl)methanone ((py)C(ph)$=$O) catalyzed by $FeCl_3$ [16], which is a well-known Lewis acid for accelerating the hydrolysis reaction, then the generated phenyl(pyridin-2-yl)methanone was reduced to form the (py)C(ph) O$^-$ ligand.

Treatment of $Fe(OAc)_2$ with (py)C(ph)NOH in EtOH led to the formation of **2** (Scheme 2). Apparently, reaction of the same ligand (py)C(ph)NOH with the different iron salts generated the different complexes, demonstrating the synthetic novelty of this work.

The molecular structures of complexes **1** and **2** are determined by single crystal X-ray diffraction [17,18]. Complex **1** consists of a V-shaped trinuclear cation $[Fe_3\{(py)C(ph)O\}_4Cl_4]^+$ and one $[FeCl_4]^-$ ion for charge balance. Fig. 1 shows the cation structure of complex **1** with a labeling scheme. The coordination environments of the two terminal $Fe^{III}$ atoms (Fe1 and Fe1′) are identical, and different from that of the central $Fe^{III}$ atom (Fe2). The terminal Fe1(Fe1′) atom is coordinated by two bridged deprotonated hydroxyl oxygen atoms originated from two (py)C(ph)O$^-$ ligand, one nitrogen atom originated from one (py) C(ph)O$^-$ ligand and two Cl$^-$ ions. The central $Fe^{III}$ atom is coordinated by four bridged deprotonated hydroxide oxygen atoms originated from four (py)C(ph)O$^-$ ligand, two nitrogen atoms originated from two (py) C(ph)O$^-$ ligands.

The geometry around the central $Fe^{III}$ atom in the trimeric unit is best described as a distorted octahedron having a $N_2O_4$ coordination environment, while the terminal two $Fe^{III}$ ions have square-pyramidal $NO_2Cl_2$ environments. The $Fe_3^{III}$ cluster can be considered as an “inverted V shape”, with Fe1 ⋯Fe2, Fe1′ ⋯ Fe2, and Fe1 ⋯ Fe1′ distances being 3.15, 3.15, and 5.53 Å, respectively, and the metal–metal–metal [Fe1-Fe2-Fe1′] bite angle being 122.59°. The {Fe1(μ-O)(μ-O)Fe2} motif

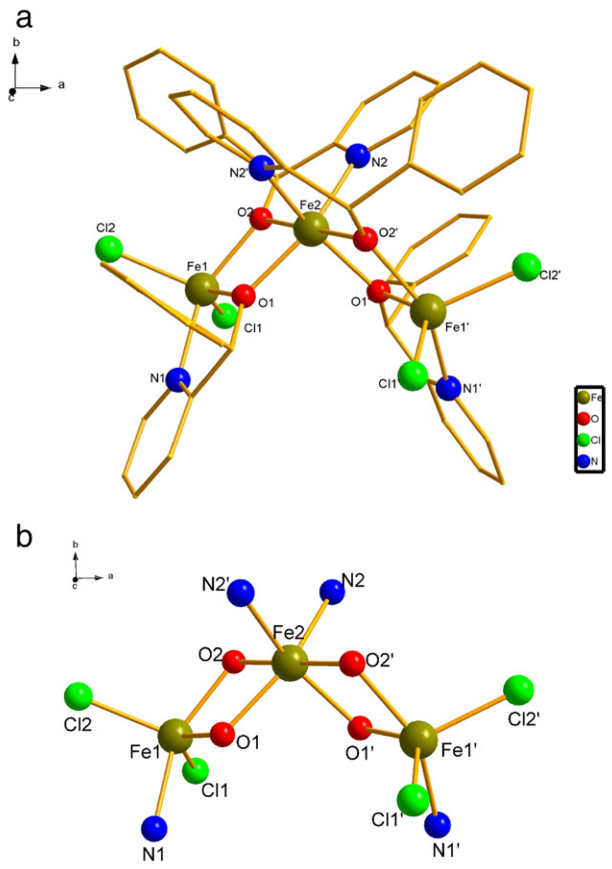


**Fig. 1.** (a) View of cation structure $[Fe_3\{(py)C(ph)O\}_4Cl_4]$ of **1**, all H atoms are omitted for clarity. (b) Coordination environments of the $Fe^{III}$ ions in **1**.

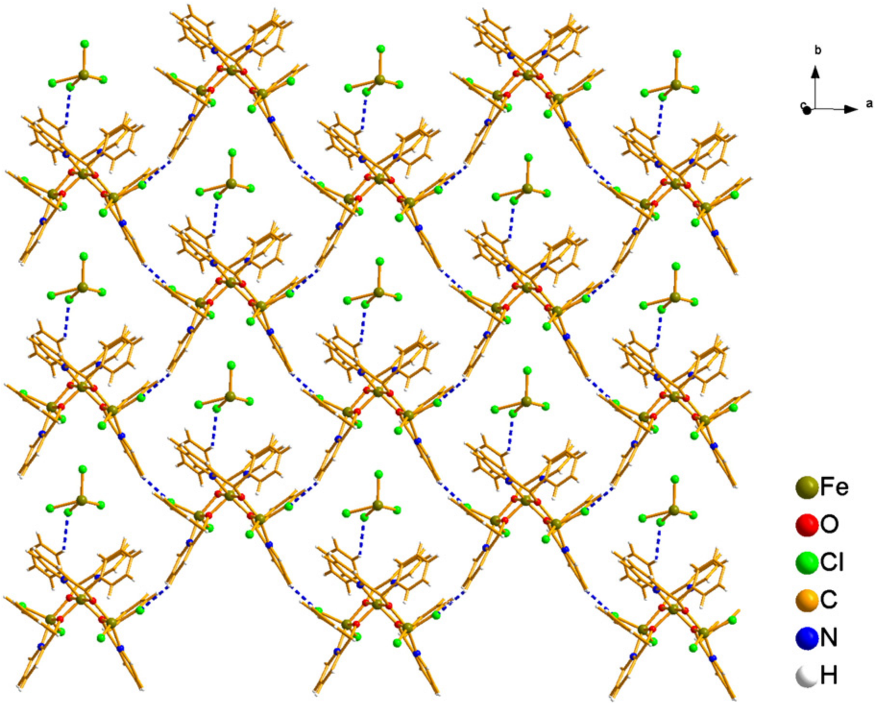


**Fig. 2.** Crystal packing diagram of complex **1**. Hydrogen contacts are represented by dotted lines.

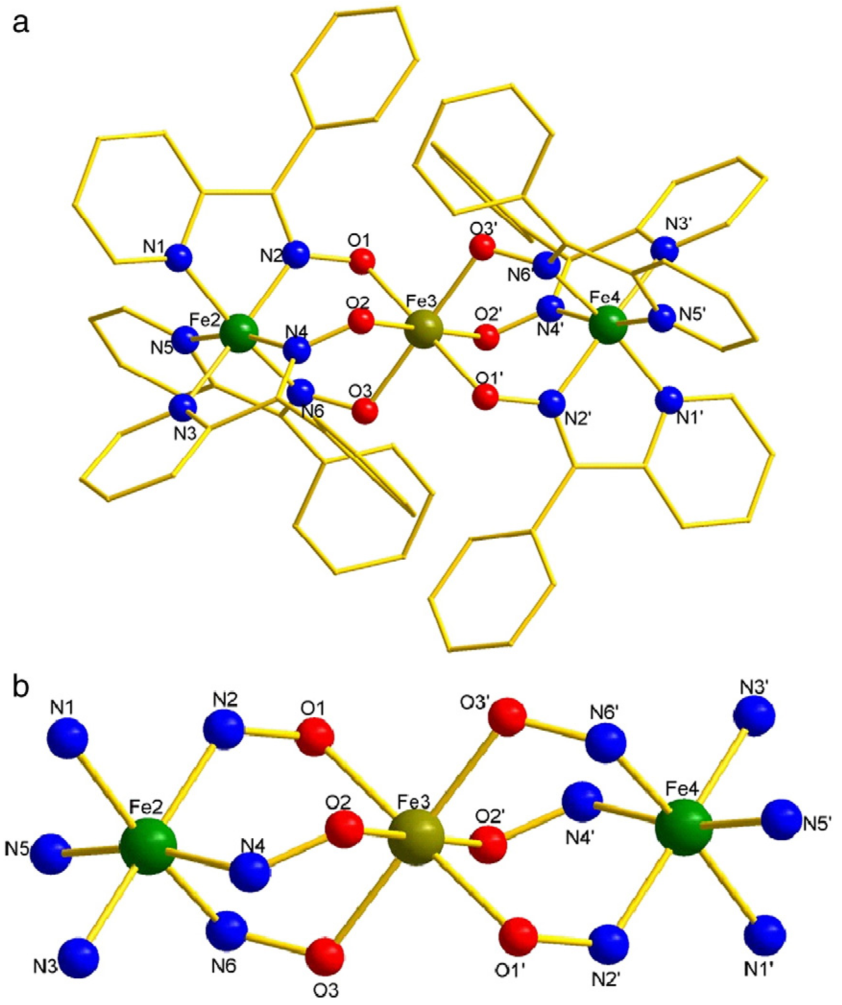


**Fig. 3.** (a) View of cation structure $[Fe_3\{(py)C(ph)NO\}_6]^+$ of **2**, all H atoms are omitted for clarity. (b) Coordination environments of the metal ions in **2**.

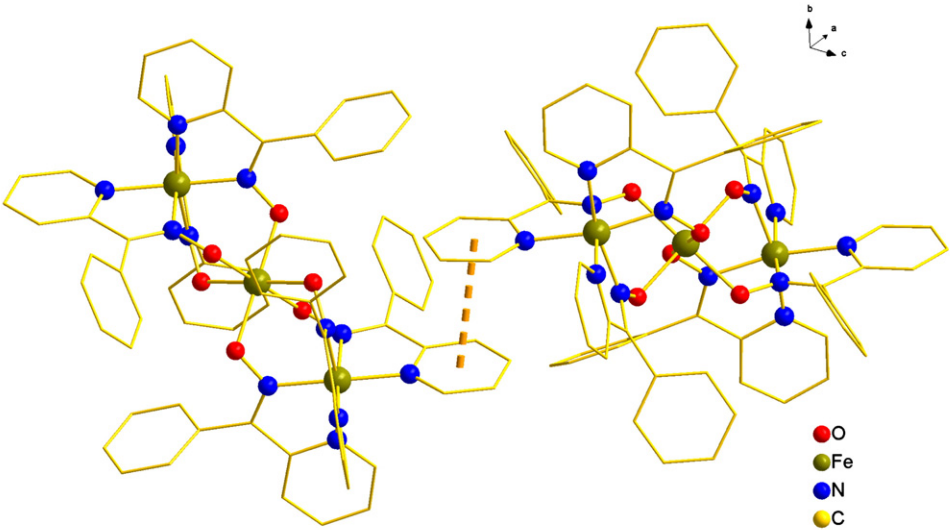


**Fig. 4.** Crystal packing in complex **2**. The π…π stacking interaction is indicated by dotted lines.

is asymmetrical, with Fe1–O1, Fe2–O1, Fe1–O2, and Fe2–O2 bond distances being 1.967(3), 1.986(3), 1.992(3), and 1.969(3) Å, respectively. As shown in Fig. 2, complex **1** features intramolecular C-H…Cl hydrogen contacts between CH group of phenyl ring as hydrogen atom donor and chloride atom from $[FeCl_4]^-$ anion as acceptor (C15-H15…Cl6, C to Cl distance 3.449(7) Å, C15-H15…Cl6 angle 128°, symmetry operation $1-x, 1+y, 1/2-z$). In addition, noticeable intermolecular C-H…Cl contacts (C18-H18…Cl2, C to Cl distance 3.429(4) Å, C18-H18…Cl2 angle 127°, symmetry operation $1/2-x, -1/2+y, 1/2-z$) are presented from CH group of the pyridyl-ring (donor) to the coordinated chloride atom (acceptor). These hydrogen contacts connect the molecules to generate infinite 2D network.

The X-ray single crystal determination reveals that complex **2** consists of a linear trinuclear cation, and one $CH_3COO^-$ ion to compensate the positive charge of the cation. As shown in Fig. 3, the central metal ion, Fe3, which is located on a crystallographic inversion centre, is octahedrally coordinated by six oxygen atoms which belong to six (py)C(ph)$NO^-$ ligands. The two terminal $Fe^{III}$ ions also adopt octahedral geometries, with the six sites on each Fe ion is occupied by the nitrogen atoms of three (py)C(ph)$NO^-$ ligands.

Charge considerations indicate that two Fe ions of **2** are in 2+ valence states and the central Fe ion is in 3+ valence state [19]. The terminal metal ions are clearly low-spin $Fe^{II}$ ions based on their Fe–N bond lengths (all <1.96 Å), which are similar to $Fe^{II}$–N bond lengths in other structurally characterized $Fe^{II}$ complexes with N-ligation. The central iron atom has all six Fe–O distances of 2.018–2.036 Å indicating its 3+ valence state. Each ligand chelates one $Fe^{II}$ ion through the 2-pyridyl and the oximate nitrogen atoms forming a five-membered chelating ring, and bridges this metal center with the central $Fe^{III}$ ion through the terminally ligated, deprotonated oxygen atom. Strong π…π stacking interactions with a centroid-to-centroid distance between pyridyl-rings of 3.57 Å are observed in the crystal, forming a "dimmer" structure (Fig. 4).

Magnetic property studies on polynuclear metal complexes are of continuing interest for coordination chemists since they can provide the understanding of fundamental factors governing their magnetic

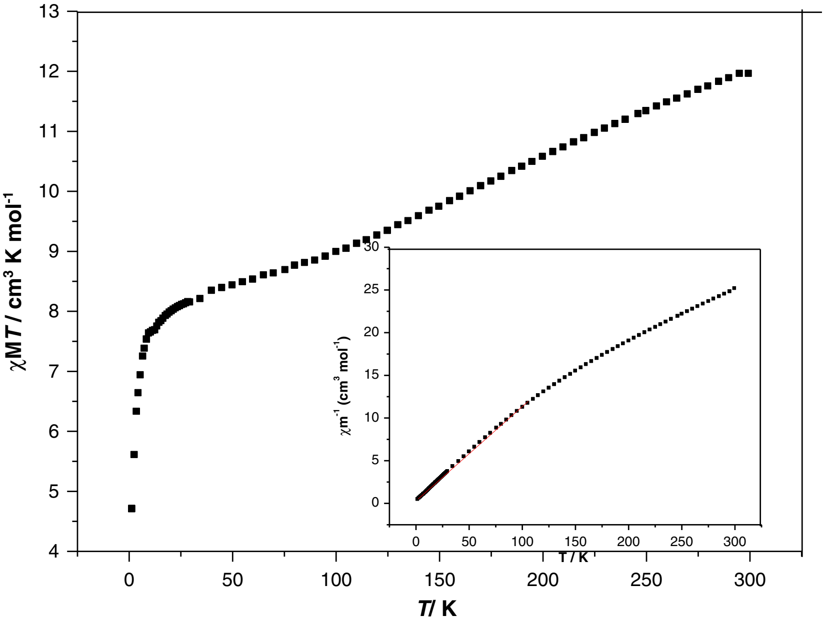


**Fig. 5.** Temperature dependence of magnetic susceptibilities in the form of $\chi_M T$ vs $T$ for **1** at 1 kOe. Inset: Temperature dependence of magnetic susceptibilities in the form of $\chi_M^{-1}$ vs $T$ for **1** at 1 kOe. The solid line corresponds to the best fit from 150 K to 2 K.

**Table 1**
Selected experimental and calculated bond lengths/A˚ and angles/ for complex **1**.

| | Exptl. | Calcd. |
|---|---|---|
| Fe1-O1 | 1.967(3) | 1.990 |
| Fe1-O2 | 1.992(3) | 2.030 |
| Fe2-O1 | 1.986(3) | 2.026 |
| Fe2-O2 | 1.969(3) | 1.989 |
| Fe1-Fe2-Fe1′ | 122.59 | 126.85 |

properties. The dc magnetic property for **1** was measured in the temperature range of 2–300 K at the applied magnetic field of 1000 Oe. The obtained data are shown in Fig. 5 in the $\chi_M T$ vs $T$ and $\chi_M^{-1}$ $v$ $T$ forms.

The $\chi_M T$ value is 11.94 cm$^3$ mol$^{-1}$ K at 300 K, slightly smaller than the spin-only value (13.13 cm$^3$ mol$^{-1}$ K) expected for three magnetically isolated high-spin Fe$^{III}$ ions ($S = 5/2$, $g = 2.00$), indicating the presence of weak antiferromagnetic interactions. Upon cooling, $\chi_M T$ value decreases gradually and reaches to 8.19 cm$^3$ mol$^{-1}$ K at 35 K, and then decreases steeply to 4.68 cm$^3$ mol$^{-1}$ K at 2 K.

The magnetic properties were tried to be analyzed by the Hamiltonian $E(S_T,S_{23}) = -J[S_T(S_T+1) - S_{23}(S_{23}+1)]$ [20], but no reasonable parameters were obtained. The magnetic data of $\chi_M^{-1}$ $v$ $T$ from 2 to 150 K (linear part) was then fitted by the Curie–Weiss law.

The Curie–Weiss fitting of the magnetic data yields $C = 9.04$ cm$^3$ mol$^{-1}$ K and $\theta = -2.57$ K, indicating the presence of weak antiferromagnetic exchange coupling interactions among the metal centers.

To gain insight into the magnetic exchange mechanism, complex **1** was selected for representative DFT calculations [21]. The cation geometry of the crystal structure was fully optimized (B3LYP functional [22]; 6–31 G* basis set for C, H, N, O, and Cl atoms; effective core potentials (LANL2DZ) for Fe atoms; gas phase). The DFT calculated bond lengths and angles of **1** agree sufficiently well with the experimentally observed ones (Table 1).

The spin density distributions for the high-spin state (16-et, S = 5/2 for each Fe$^{III}$ ion) are illustrated in Fig. 6. It can be seen that, the spin density is localized mainly on the three iron(III) centers and four terminal Cl anions, which could be considered as reasonable in a "V-shaped" environment. In addition, the magnetic exchange pathway is primarily mediated by the bridging $\mu_3$-O atoms from (py)C(ph)NOH ligands, and these mediators support an antiferromagnetic interaction.

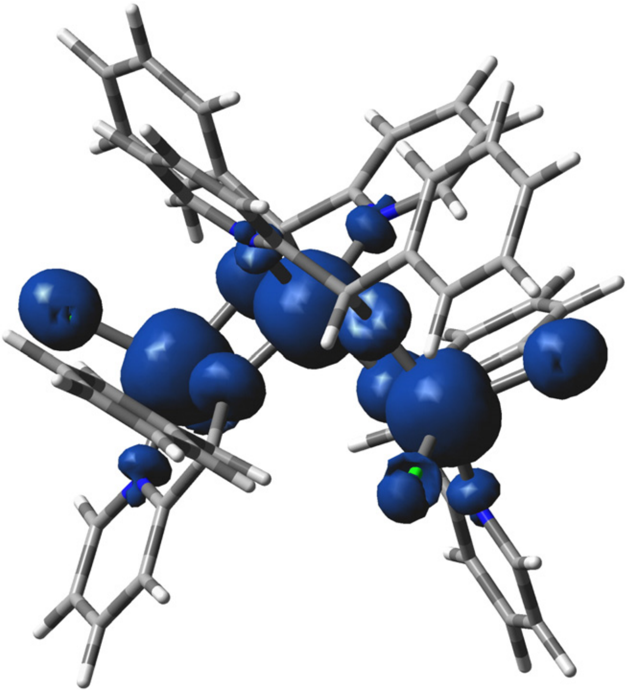


**Fig. 6.** Spin density for the cation of complex **1** (contour value 0.006 a.u.).

In summary, two polynuclear iron complexes of the compositions [$Fe_3\{(py)C(ph)O\}_4Cl_4$][$FeCl_4$] (**1**) and {[$Fe_3\{(py)C(ph)NO\}_6$][$CH_3COO$] (**2**) have been synthesized by solvothermal reaction, and characterized by X-ray single crystal diffraction, IR spectroscopy, and elemental analysis. The (py)C(ph)O$^-$ ligand of complex **1** was formed by the $FeCl_3$ catalyzed *in situ* metal ligand reaction. The work described above also demonstrates the synthetic novelty that arises when solvothermal techniques are used in Fe$^{II}$/2-pyridyl oxime chemistry. Magnetic property measurement indicates that there exist weak antiferromagnetic interactions between the magnetic centers in **1**. Magneto-structural correlation was investigated by theoretical calculations, which suggested the observed magnetic behaviors were due to the $\mu_3$-O atoms from (py)C(ph)NOH ligands in the bridging pathway. These results indicate that the phenyl-pyridine-2-yl-methanone oxime ligand is a useful linkage for the synthesis and design of new functional materials.

## Acknowledgements

The authors appreciate the financial supports of Hundreds of Talents Program (2005012) of CAS, Natural Science Foundation of China (20872105), "Qinglan Project" of Jiangsu Province (Bu109805) and A Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions.

## Appendix A. Supplementary material

CCDC 841776 and 848421contain the supplementary crystallographic data for complexes **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data to this article can be found online at doi:10.1016/j.inoche.2012.01.015.

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[18] *Crystallographic analysis of* ***2*** *($C_{156}H_{138}N_{24}Fe_6O_{20}$)*: $M = 3004.00$, Monoclinic, *P21/n*, crystal size $0.24 \times 0.23 \times 0.20$ mm, $V = 6833.7(3)$ Å$^3$, $a = 16.1295(4)$ Å, $b = 23.3839(6)$ Å, $c = 18.1708(4)$ Å, $\beta = 94.35(10)°$, $T = 296(2)$ K, $Z = 2$, $\rho_{cal} =$ 1.460 Mg/m$^3$, Mo K($\alpha$1) = 0.71073 Å. 65728 reflections measured, of which 16928 were unique. $R1 = 0.\ 0487$, $wR2 = 0.1250$, GooF = 1.016. The structure was solved by direct methods (SHELXS-97) and refined with SHELXS-97.

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