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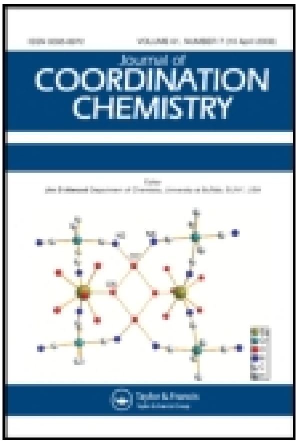

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Synthesis, crystal structure, and magnetic properties of a new Fe(II) complex with reduced radical ligands

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Synthesis, crystal structure, and magnetic properties of a new Fe(II) complex with reduced radical ligands

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A new Fe(II) complex, $[Fe(HIM2Py)_2(N(CN)_2)_2] \cdot 2H_2O$ (HIM2py = 1-hydroxyl-2(2′-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1 *H*-imidazole), has been synthesized and characterized. The X-ray analysis reveals that HIM2py ligands are coordinated to iron as an unusual six-membered bidentate chelate with κ^2N(py), O(HIM) mode. The variable-temperature magnetic susceptibility suggests that weak antiferromagnetic interactions exist in the complex.

Keywords: Fe(II) complex; Reduced nitroxide radical; Crystal structure; Magnetic properties

1. Introduction

In the field of molecular magnetic materials, combination of transition metal ions with nitronyl nitroxide radicals has become a very active focus [1–9]. Nitronyl nitroxides have been extensively used as building blocks for pure organic ferromagnets [10–13] and as bridging ligands for paramagnetic metal ions [14, 15] owing to their exceptional stability and ease of chemical modification. Meanwhile, discrete complexes, with definite geometry resulting from paramagnetic metal ions and organic radicals, are good candidates for fundamental studies of magneto-structural correlation, in particular how structural factors affect the metal–organic radical interactions [16–18]. Such investigation is necessary not only for understanding the magnetic exchange mechanism between the metal and organic radical but also for guiding the design of new organic radical ligands for the development of molecular-based magnetic materials [19]. Therefore, chemists pay much attention to the design of different kinds of metal–radical complex architectures with appropriate organic nitronyl nitroxide radicals and coligands. A large number of metal–radical complexes with various structures have been synthesized and magnetically characterized [20–23]. However, Fe(II)–radical complexes are very scarce; to the best of our knowledge, there are only two reports on Fe(II) complexes with nitroxide radicals [24, 25]. Very recently, we used Fe(II) and IM2py ligands to obtain three Fe(II) complexes in which the IM2py became HIM2py

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because of one electron reduction of the N–O radical moiety. In this article, with the same nitronyl nitroxide radical ligand, we synthesized another Fe(II) complex, $[Fe(HIM2Py)_2(N(CN)_2)_2] \cdot 2H_2O$ (HIM2py = 1-hydroxyl-2(2′-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1 *H*-imidazole), and describe the crystal structure and magnetic properties.

2. Experimental

2.1. *Materials and instrumentation*

All reagents were purchased from commercial sources and used as received. 2-(2′-Pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1 *H*-imidazole-1-oxyl (IM2py) was prepared by the literature method [26]. Diffraction data were collected at 113 K with a Bruker SMART 1000 CCD diffractometer. Elemental analyses for C, H, and N were carried out with a Perkin-Elmer 240 elemental analyzer. Infrared (IR) spectra were recorded in KBr pellets from 4000 to 400 cm^{-1} on a Bruker Tensor 27 IR spectrometer. Variable-temperature magnetic susceptibilities were measured on a MPMS XL-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms.

2.2. *Preparation of the complex*

$[Fe(HIM2Py)_2(N(CN)_2)_2] \cdot 2H_2O$: an aqueous solution (5 mL) containing IM2py (0.109 g, 0.5 mmol) and $NaN(CN)_2$ (0.045 g, 0.5 mmol) was added to an aqueous solution (10 mL) of $Fe(ClO_4)_2 \cdot 6H_2O$ (0.0908 g, 0.25 mmol) (and a pinch of ascorbic acid). The mixture was stirred for 0.5 h and allowed to stand in a refrigerator for several days to give red single crystals suitable for X-ray diffraction studies. Yield: 0.108 g (65%). Anal. Calcd for $C_{28}H_{38}FeN_{12}O_4$ (%): C, 50.76; H, 5.78; N, 25.36. Found (%): C, 50.83; H, 5.80; N, 25.40. IR data (KBr, cm^{-1}): 2157(s), 2220(s), 2253(s), 3495 (m), 3290 (m), 1453(m), 1120 (m), 635(m).

2.3. *X-ray crystallography*

Diffraction data for the complex were collected at 113 K with a Bruker SMART 1000 CCD diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å) with the ω–2θ scan technique. An empirical absorption correction (SADABS) was applied to raw intensities [27]. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXS 97 [28] and SHELXL 97 [29], respectively. Non-hydrogen atoms were refined anisotropically and hydrogens were added theoretically, riding on the concerned atoms and refined with fixed thermal factors. Detailed crystallographic data for the complex are listed in table 1 and selected bond lengths and angles are listed in table 2.

Table 1. Crystal data and structure refinements for the complex.

Empirical formula	$C_{14}H_{19}Fe_{0.50}N_6O_2$
Formula weight	331.28
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	
a	13.6539(12)
b	8.4326(6)
c	14.3314(14)
β	100.670(4)
Volume (Å^3)	1621.6(2)
ρ_{calc} (g cm^{-3})	1.357
F (000)	696
Crystal size (mm^3)	$0.12 \times 0.10 \times 0.08$
θ range for data collection (°)	2.85–25.01
h, k, l range	$-16 \leq h \leq 16$, $-10 \leq k \leq 10$, $-16 \leq l \leq 17$
I_{hkl} collected/unique	11,669/2809
R_{int}	0.1108
Data/restraints/parameters	2809/2/218
Goodness-of-fit on F^2	1.154
R_1, wR_2 [$I > 2\sigma(I)$]	0.0847, 0.1487
R_1, wR_2 (all data)	0.1089, 0.1596
Maximum difference peak and hole (e Å^{-3})	0.301 and −0.455

Table 2. Bond lengths (Å) and angles (°) of the complex.

Fe(1)–O(1)	2.029(3)	N(1)–C(1)	1.346(5)
Fe(1)–N(1)	2.215(4)	C(1)–C(2)	1.390(6)
Fe(1)–N(5)	2.138(4)	N(3)–H(3)	0.8800
N(2)–O(1)	1.338(4)	–	–
O(1)–Fe(1)–N(1)	84.3(1)	N(2)–O(1)–Fe(1)	116.6(2)
O(1)–Fe(1)–N(5)#1	88.5(1)	C(5)–N(1)–Fe(1)	118.1(3)
O(1)–Fe(1)–N(5)	91.5(1)	C(1)–N(1)–Fe(1)	125.2(3)
O(1)–Fe(1)–N(1)#1	95.7(1)	O(1)–N(2)–C(7)	119.7(3)
N(5)–Fe(1)–N(1)	87.9(1)	O(1)–N(2)–C(6)	127.8(4)
N(5)–Fe(1)–N(1)#1	92.1(1)	–	–

Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $-y+2$, $-z+1$.

3. Results and discussion

3.1. *[Fe(HIM2Py)$_2$(N(CN)$_2$)$_2$]·2H$_2$O*

The complex crystallized in the monoclinic space group $P2_1/c$ and the labeling scheme for the crystal structure is depicted in figure 1. X-ray crystallography shows that HIM2py coordinates to Fe(II) in an unusual six-membered chelate κ^2N(py), O(HIM) mode, namely binding to the metal center through the imino *via* oxygen and pyridyl nitrogen, forming a *trans*-MN_2O_2 unit. The complex is centrosymmetric and the Fe(II) has a distorted octahedral geometry with the equatorial plane comprising both nitrogens (N(1), N(1 A)) and oxygens (O(1), O(1 A)) from two HIM2py ligands; nitrogens (N(5), N(5 A)) from two dicyanamide anions are axially ligated. The bond lengths of the Fe–O(HIM2py) and Fe–N(pyridyl) are 2.021(3) and 2.214(4) Å, respectively, while that of Fe–N(N(CN)$_2$) is 2.139(4) Å, showing the corresponding axial bond distance longer than equatorial average bond distance. The structure is

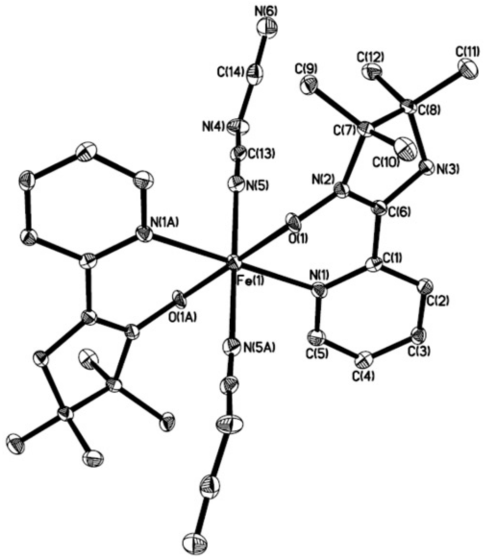
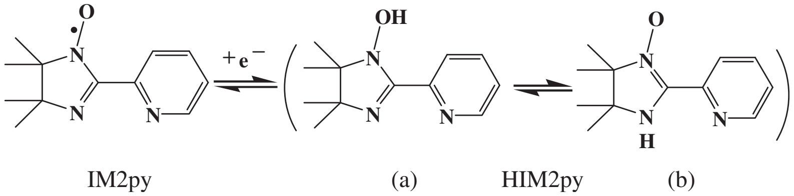


Figure 1. An ORTEP drawing of the complex with atom-labeling and 30% thermal ellipsoids.

Table 3. Bond lengths (Å) of reported complexes.

Complex	Fe–L(equatorial site)	Fe–L(axial site)	N–O(HIM2py)
$[Fe(HIM2py)_2(SCN)_2]$	2.040(3) 2.217(3)	2.168(4)	1.333(4)
$[Fe(HIM2py)_2(H_2O)_2](ClO_4)_2 \cdot 2H_2O$	2.083(2) 2.235(3)	2.187(3)	1.367(3)
$[Fe(HIM2Py)_2(N(CN)_2)_2] \cdot 2H_2O$ (this work)	2.021(3) 2.214(4)	2.139(4)	1.338(4)



Scheme 1. The formation of the reduction of the imino radicals.

similar to our previous report on Fe(II) complexes with the same reduced radical ligand, whose results are listed in table 3. The bond length of N(2)–O(1) is 1.338(4) Å, much longer than the N–O bond length in IM2py coordinated complex; this is clearly indicative of the reduced form in scheme 1(b) with amidinooxide imidazoline group derived from IM2py, while the corresponding distance in nitroxide ranges from 1.25 to 1.32 Å [30]. The redox process of IM2py is shown in scheme 1, showing that the reduced radical can exist in two tautomeric forms [26, 31], imino-hydroxylamine and amidinooxide. The mechanistic details of the reduction of the imino radicals are not completely clear, and it is likely that the formation of HIM2py is favored both by

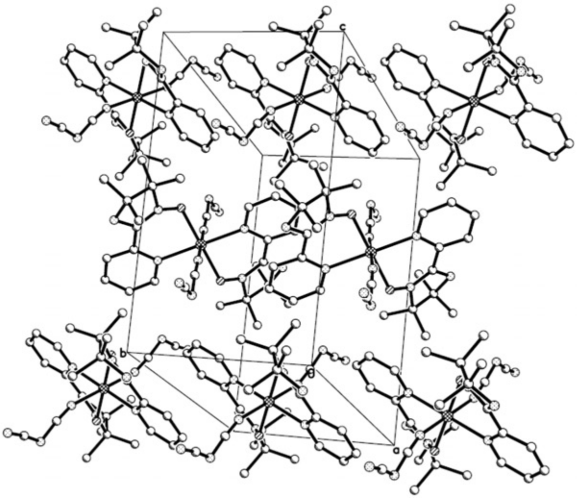


Figure 2. The crystal packing of the complex. All hydrogens are omitted for clarity.

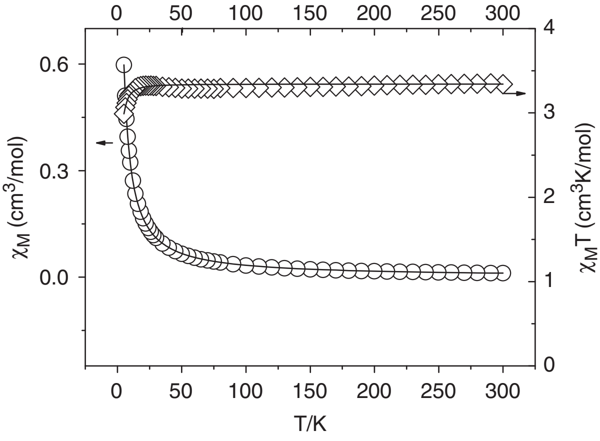


Figure 3. The plots of χ_M (○) and $\chi_M T$ (◇) *vs*. T for the complex, the solid line shows the best fit to the value.

ascorbic acid and standing for a long time [31]. The dihedral angle between the reduced imino nitroxide moiety (O(1), N(2), C(6), N(3)) and the pyridine ring of the radical is 25.69°, whereas the mean equatorial plane (O(1), Fe(1), N(1)) shows an angle of 37.11° with the reduced imino nitroxide moiety (O(1), N(2), C(6), N(3)). The packing diagram of the complex is shown in figure 2.

3.2. *Magnetic properties*

Variable-temperature magnetic susceptibility data of the complex were measured from 2 to 300 K under applied magnetic field of 2000 G. Figure 3 shows the temperature dependences of χ_M and $\chi_M T$ for the complex. The observed value of $\chi_M T$ is

3.34 cm^3 K mol^{-1} at 300 K, which is obviously larger than the spin-only value of 3 cm^3 K mol^{-1} for $S = 2$, indicating an unquenched orbital contribution. Upon cooling from 300 to 30 K, the value of $\chi_M T$ is almost consistent, which is clearly indicative of weak magnetic interaction, and then decreases slowly below 30 K. Significant zero-field splitting of the single-ion ground-state quintet is evident in the low temperature data. For octahedral Fe(II) complexes, the electronic ground state is orbitally degenerate ($^5T_{2g}$) and there exists important orbital contribution. The magnetic behavior of mononuclear Fe(II) complexes should be interpreted assuming λ(spin–orbit parameter) and/or the *D*(zero-field splitting parameter) in the corresponding formulae. Only, when the distortion of the coordination geometry is low, one can simultaneously use the *D* and λ parameters. Thus, the experimental data have been fitted to the formula for an $S = 2$ mononuclear system with *D* parameter [32]:

$$\chi_{\parallel} = C(2e^{-x} + 8e^{-4x})/(1 + 2e^{-x} + 2e^{-4x}),$$
$$\chi_{\perp} = C[(6/x)(1 - e^{-x}) + 4/3x(e^{-x} - e^{-4x})]/(1 + 2e^{-x} + 2e^{-4x}),$$
$$\text{with } \chi_M = (\chi_{\parallel} + 2\chi_{\perp})/3,\ C = Ng^2\beta^2/kT \text{ and } x = D/kT.$$

The weak molecular interaction was considered in mean-field approximation as zJ'.

$$\chi_{\text{total}} = \chi_M/[1 - \chi_M(zJ'/Ng^2\beta^2)].$$

The best agreement between calculated and experimental values of the susceptibility were found with $g = 2.11$, $|D| = 2.63\ \text{cm}^{-1}$, $zJ' = -0.02\ \text{cm}^{-1}$, the agreement factor $R = 1.02 \times 10^{-5}$ ($R = \Sigma(\chi_M^{\text{Calcd}} - \chi_M^{\text{Obsd}})^2/(\chi_M^{\text{Obsd}})^2$). The fitting data are consistent with those of our previous report on Fe(II) complexes [33] and are all in agreement with the literature reported for Fe(II) complexes [34].

Fe(II) ions in octahedral environments show significant single-ion anisotropies or spin-orbital couplings. The spin-orbital coupling together with the usual distortion with regard to octahedral symmetry creates a zero-field splitting (*D*), whose magnitude is very high for strongly distorted Fe(II) complexes. Although the Fe1–N1, Fe1–N5, and Fe1–O1 distances are slightly different, the N5–Fe1–N1 and N5–Fe1–O1 angles are nearly 90° (87.9 and 88.5°, respectively). This feature can explain why the calculated *D* parameter is only 2.63 cm^{-1}. This value is slightly smaller than those (3.69, 5.99 cm^{-1}, respectively) of our previous report on the similar Fe(II) complexes with the same reduced radical ligand [33], which suggests that the complex in this article is more symmetric.

In summary, a new Fe(II) complex with reduced radical ligand HIM2py-κ^2N(py), O(HIM) was obtained at room temperature. It has been characterized structurally as well as magnetically. The crystal structure analyses indicate that HIM2py coordinates to iron in an unusual six-membered bidentate chelate mode. The magnetic properties reveal that there is a weak antiferromagnetic interaction in the molecule. The nitronyl nitroxide ligand IM2py becoming its reduced form, HIM2py, will inspire new ideas in designing Fe(II)–radical complexes by changing conditions.

Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 799814. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (Fax: +44 1223336 033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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