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Preparation and characterization of carboximidate iron(II) complexes

Liyi Chen [a], Wen Zhang [a], Shuping Huang [b], Xianglin Jin [c], Wen-Hua Sun [a,*]

[a] *Laboratory of Engineering Plastics, Joint Laboratory of Polymer Science and Materials, The Chinese Academy of Sciences, Institute of Chemistry, Zhongguancun, Beiyijie, Beijing 100080, PR China*
[b] *School of Chemistry and Chemical Engineering, Shanxi University, Taiyuan 030006, PR China*
[c] *Institute of Physical Chemistry, Peking University, Beijing 100871, PR China*

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Abstract

The reactions of $C_5H_4NCH{=}NNHC({=}O)Ph$ (**1**) with Fe(II) chloride gave $[Fe_2(C_5H_4NC(OEt){=}NNHC({=}O)Ph)_2(\mu\text{-}OEt)_2Cl_2])$ (**2**) in ethanol and $[Fe_2(C_5H_4NC(OMe){=}NNHC({=}O)Ph)_2(\mu\text{-}OMe)_2Cl_2]$ (**3**) in methanol as well as $[Fe(C_5H_4NCH{=}NNHC({=}O)Ph)Cl_2]$ (**4**) in tetrahydrofuran, respectively. The X-ray diffraction analysis reveals their structures and complex **4** is proposed as an intermediate of formation of complexes **2** and **3**.

Keywords: Carboximidate; Fe(II) complex; Crystal structure

Imino-containing compounds have drawn much attention due to their biological activities and organic synthesis considerations [1–3]. Because of the pharmaceutical applications, the structure unit of carboximide ester has recently been explored as a useful intermediate in organic syntheses [4–7]. A distinct example was forming copper complexes containing benzoylpyridin-2-yl-methylene-hydrazide derivatives [8]. In this paper, the extensive reactions of $C_5H_4NCH{=}NNHC({=}O)Ph$ (**1**) [9] with Fe(II) chloride in various solvents give three complexes **2**–**4** (Scheme 1).

Benzoylpyridin-2-yl-methylene-hydrazide (**1**) reacted with stoichiometric amount of $FeCl_2 \cdot 4H_2O$ to form complexes **2** in ethanol, **3** in methanol and **4** in tetrahydrofuran (THF), respectively. The complex **4** reacted with alcohol to form the complexes **2** and **3**. Their crystals were obtained by diffusing ethyl ether into the reactant solution.

All complexes were carefully investigated by elemental analysis, spectral characterization as well as single-crystal determination. According to complexes **2** [1] and **3** [2], the infrared spectra showed the lower frequency

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[*] Corresponding author. Tel.: 86 10 62557955; fax: +86 10 62618239.
E-mail address: whsun@iccas.ac.cn (W.-H. Sun).

[1] Complex **2**. Brown crystals, 11%. $C_{34}H_{40}N_6O_6Fe_2Cl_2$ Calc. (found): C, 50.33 (50.27); H, 4.97 (4.74); N, 10.36 (10.34). IR (cm^{-1}, KBr): 2964 (w), 2931 (w), 2878 (w, CH_3, CH_2), 1632 (s) (C═O), 1511 (m, C═N), 1371 (s), 1322 (s, C—O—C). M_p: >300 °C. $\mu_{eff} = 4.40$ μ_B. $M = 811.32$, orthorhombic, $a = 18.535(4)$, $b = 10.503(2)$, $c = 18.433(4)$ Å, $V = 3588.4(12)$ $Å^3$, $T = 293(2)$ K, Space group Pbcn, $Z = 4$, number of collected reflections = 21837, number of independent reflections = 4060, $R(F^2) = 0.0388$, $wR = 0.0552$. Full crystallographic detail was deposited at the Cambridge Crystallographic Data Centre with number CCDC 220810.

[2] Complex **3**. Brown crystals, 33%. $C_{30}H_{32}N_6O_6Fe_2Cl_2$ Calc. (found): C, 47.71 (47.72); H, 4.27 (3.98); N, 11.13 (11.02). IR (cm^{-1}, KBr): 2958 (w), 2922 (w), 2818 (w, CH_3), 1631 (s, C═O), 1511 (m, C═N), 1375 (s), 1335 (s, C—O—C). M_p: >300 °C. $\mu_{eff} = 4.46$ μ_B $M = 755.22$, monoclinic, $a = 11.125(2)$, $b = 9.2402(18)$, $c = 16.402(3)$ Å, $\beta = 100.67(3)$, $V = 1656.9(6)$ $Å^3$, $T = 293(2)$ K, Space group P2(1)/*c*, $Z = 2$, number of collected reflections = 5076, number of independent reflections = 2887, $R(F^2) = 0.0291$, $wR = 0.0232$. Full crystallographic detail was deposited at the Cambridge Crystallographic Data Centre with number CCDC 220811.

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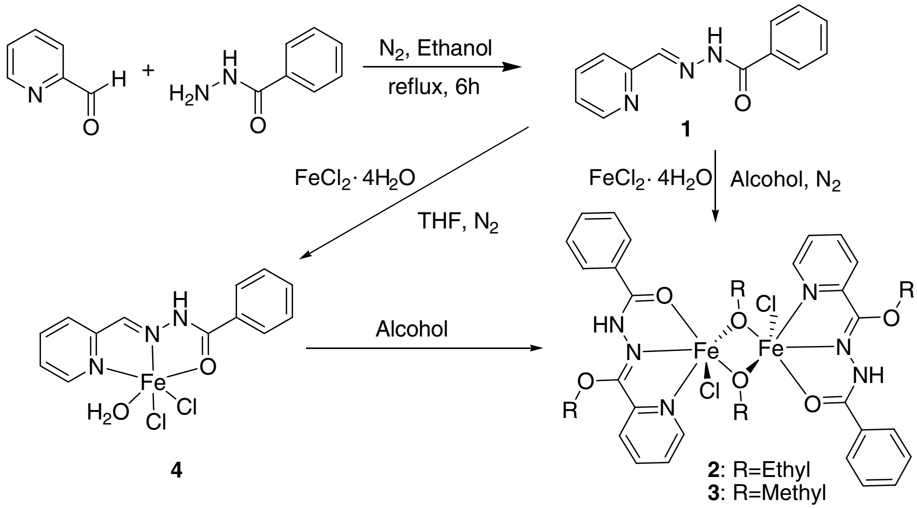

Scheme 1. Synthesis of compounds.

and intensity for ν(C=O) of the complexes (1632 cm^{-1} for **2**; 1631 cm^{-1} for **3**) compared to the ligand **1** (1684 cm^{-1}), this confirmed the coordination of C=O with Fe(II). Due to the coordination of nitrogen atom in the both complexes, the bands of ν(C=N) also shift (1532 cm^{-1} for **1**; 1511 cm^{-1} for **2**; 1511 cm^{-1} for **3**). In addition, several new absorptions appeared between 2800 and 2960 cm^{-1} (ν(—CH_3, —CH_2)) and 1320–1375 cm^{-1} (ν(C—O)) for the complexes. In their single crystal structures, the complexes **2** and **3** both contained the two six-coordinated Fe(II) cations bridged by two alkoxy groups (Figs. 1 and 2).

Looking at the ligand moiety, a substitution reaction happens at C(6) atom by alkoxy group which is *trans* to Fe(II) ion due to the coordination of pyridine moiety. In the complex **2**, as the example, the bond between C(6) and N(1) atoms remains double bond (C(6)=N(1), 1.284(3) Å). Interestingly, the O(2)—C(6) bond length is 1.318(3) Å, much shorter than the single bond length of O(2)—C(14) (1.441(3) Å). The similar phenomena were previously observed in carboximide ester [10].

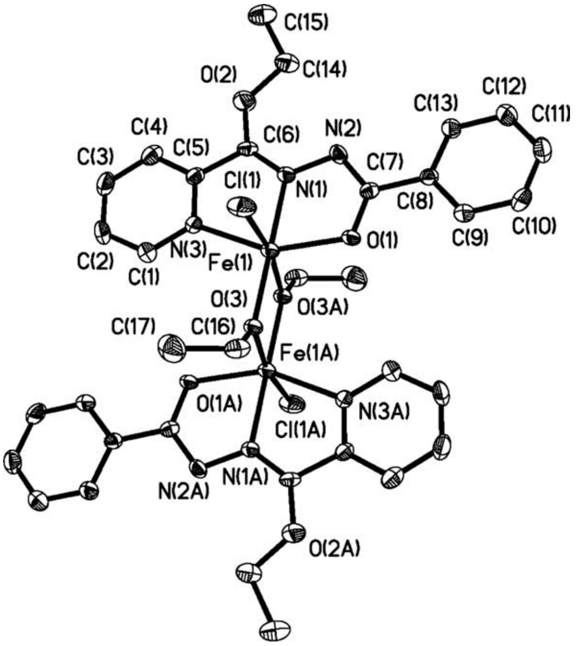

Fig. 1. Structure of complex **2**, 30% probability ellipsoids, H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Fe(1)–O(3) 1.9642(18), Fe(1)–O(3A) 2.0639(19), O(1)–C(7) 1.290(3), O(2)–C(6) 1.318(3), O(2)–C(14) 1.441(3), N(1)–C(6) 1.284(3), N(1)–N(2) 1.386(3), N(2)–C(7) 1.319(3) and O(1)–Fe(1)–N(1) 74.41(9), O(3)–Fe(1)–N(3) 102.69(9), N(1)–Fe(1)–N(3) 74.02(10), O(3A)–Fe(1)–Cl(1), 169.41(6).

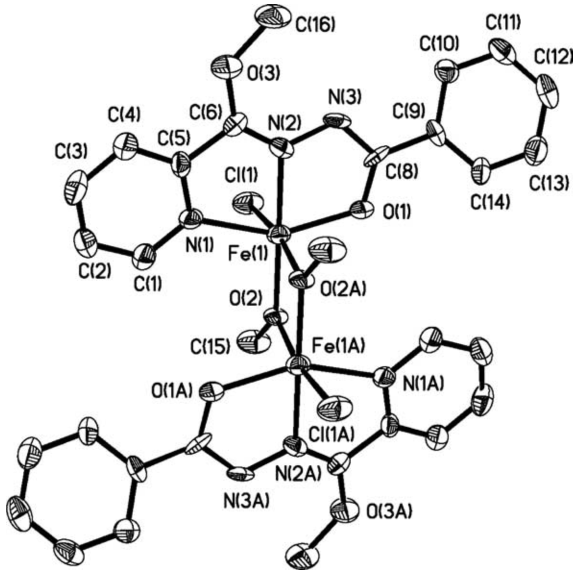

Fig. 2. Structure of complex **3**, 30% probability ellipsoids, H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Fe(1)–O(2) 1.936(2), Fe(1)–O(2A) 2.058(3), O(1)–C(8) 1.299(5), O(3)–C(6) 1.344(5), O(3)–C(16) 1.464(4), N(2)–C(6) 1.257(5), N(2)–N(3) 1.384(5), N(3)–C(8) 1.332(6) and O(2)–Fe(1)–O(1) 106.40(12), O(1)–Fe(1)–N(2) 76.66(15), O(2)–Fe(1)–N(1) 102.46(14), N(2)–Fe(1)–N(1) 72.83(16), O(2A)–Fe(1)–Cl(1), 169.95(9).

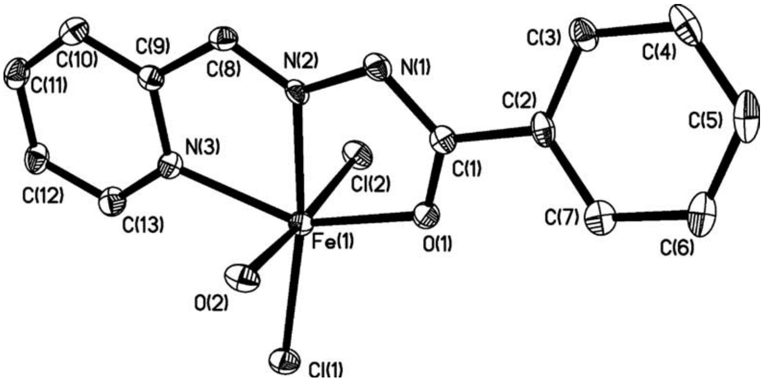

Fig. 3. Structure of complex **4**, 30% probability ellipsoids, H atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°): Fe(1)–O(1) 2.003(3), Fe(1)–N(2) 2.106(3), Fe(1)–O(2) 2.113(3), Fe(1)–N(3) 2.137(3), Fe(1)–Cl(1) 2.2335(12), Fe(1)–Cl(2) 2.3217(14), O(1)–C(1) 1.274(4), N(1)–C(1) 1.330(5), N(1)–N(2) 1.373(4), N(2)–C(8) 1.272(5) and O(1)–Fe(1)–N(2) 74.23(12), N(2)–Fe(1)–N(3) 74.35(13), O(2)–Fe(1)–Cl(1) 88.72(9).

The bond length of O(1)—C(7) (1.290(3) Å) is between the typical single bond C(sp^3)—O (1.34 Å) and double bond C(sp^2) = (1.21 Å) [11]. In addition, the N(1)—N(2) (1.386(3) Å) and N(2)—C(7) (1.319(3) Å) have part characters of double bonds, which is similar to its Cu(II) analogue reported by Pal et al. [8]. Therefore extended conjugated system is present in the resultant iron complex.

The complex **4** [3] (Fig. 3) was formed in the stoichiometrical reaction of the ligand **1** with $FeCl_2$ in THF. The complex **4** is mononuclear with a coordinated water molecule. The complex **4** reacted with ethanol or methanol to yield the complexes **2** and **3**. Therefore complex **4** is postulated as an intermediate in forming complexes **2** and **3** with nucleophilic attack of alkoxy on —CH=N of complexes **4**. The effective magnetic moment μ_{eff} of complexes **2, 3** and **4** were measured with the values of 4.40, 4.46 and 5.46 μ_{B}, respectively. It proved that those iron complexes were all high-spin species having the configuration $(t_{2g})^4(e_g)^2$.

In general, hydrazine-derived Schiff-base ligands could easily coordinated with transition metals, and the polarity of H—C bond in H—C=N—M is increased for easy substitution with alkoxy group. This helps to understand the formation of carboximide ester in the copper complexes [8], and more importantly the extensiveness to other transition metals. Therefore this provides a convenient method for the transformation of —CH=N group into carboximide ester.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.inoche.2004.10.019.

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[3] Complex **4**. Red crystals, 20%. $C_{13}H_{11}N_3OFeCl_2$ Calc. (found): C, 44.36 (44.28); H, 3.15 (3.25); N, 11.94 (11.84). IR (cm^{-1}, KBr): 1624(s, C=O), 1523 (s, C=N). M_p: 132 °C (Dec.). $\nu_{\mathrm{eff}} = 5.46\ \nu_{\mathrm{B}}$. $C_{13}H_{11}Cl_2FeN_3O \cdot H_2O$, $M = 370.01$, monoclinic, $a = 14.390(3)$, $b = 7.1480(14)$, $c = 15.002(3)$ Å, $\beta = 106.70(3)°$, $V = 1478.0(5)$ Å^3, $T = 123(2)$ K, Space group P2(1)/n, $Z = 4$, number of collected reflections = 5827, number of independent reflections = 2593, R (F^2) = 0. 0491, $wR = 0.0867$. Full crystallographic detail was deposited at the Cambridge Crystallographic Data Centre with number CCDC 220812.