ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 1, pp. 144–147. © Pleiades Publishing, Ltd., 2015.

Synthesis and Characterization of Novel Ferrocenyl Heterocyclic Compounds[1]

Xiaoju Liu[a], Guoyu Ren[a], Xiangruo Ma[a], Long Yan[a],
Yurong Jiao[a], Yajun Ma[a], and Bingqin Yang[b]

[a] *Key Laboratory of Synthetic and Natural Chemistry, Ministry of Education,*
Chemical Engineering Institute, the Yu-Lin University of Yulin,
Chongwen Avenue 4, Yulin 719000, Shaanxi Province, China

[b] *Key Laboratory of Synthetic and Natural Functional Molecule Chemistry, Ministry of Education,*
Department of Chemistry, Northwest University, Xi'an, Shannxi, China
e-mail: liuxiaoju0628@163.com

Received October 22, 2014

Abstract—An efficient synthetic approach to the synthesis of ferrocenyl heterocyclic derivatives in dilute solutions has been developed. The new compounds were characterised by means of IR, UV, and ^{1}H NMR spectroscopy and elemental analysis. The structure of complex **I** was studied by X-ray single-crystal diffraction. The synthesized compounds have a potential of new enzyme models and molecular recognition hosts.

Keywords: ferrocenyl heterocycles synthesis, characterization, X-ray analysis

DOI: 10.1134/S1070363215010247

A wide variety of ferrocene derivatives application is based on their unique structural, electronic and magnetic properties [1–6], specific electrical conductivity [7, 8], unique magnetic character [9], thermal stability [10, 11], high nonlinear optical susceptibility [12], and some others [13–19].

In the present study the novel ferrocenyl heterocyclic compounds **I–V** (Scheme 1) were synthesized starting with ferrocene and proceeding via 1,1'-diacetylferrocene [20, 21], 1,1'-ferrocene-dicarboxylic acid [22], 1,1'-ferrocene-di(carbonyl chloride) [23]. The latter was condenced with dihydroxyethyl aniline in dilute media.

RESULTS AND DISCUSSION

The products **I–V** were stable upon storage in the air for several months. All compounds exhibited the anticipated $[M + \mathrm{H}]^+$ peak in their mass spectra. The IR spectra of compounds **I–V** demonstrated bands of **I–V** (C=O) vibrations in the range 1717–1730 cm^{-1}, which was lower than in typical esters because of formation of the strong H-bond.

The complex **I** crystallized in triclinic form, space group $P1$ (Fig. 1). The dihedral angle between Cp rings is 6.13°. The C atoms in Cp rings deviate significantly from coplanarity. The torsion angles C–C–C–C in two Cp rings vary within the range from –9.08° (2.66) to – 9.36° (2.66). These data exhibit that the size and the torsional angles of cyclopentadiene diminish upon cyclization. In the same molecule the corresponding bonds C–O, C–C and C–N become different due to steric and stack interactions.

The bonds lengths in compound **I** are following: O^2–C^6 1.2277 Å (0.0238), O^4–C^{11} 1.2371 Å (0.0258), O^5–C^{30} 1.230 Å (0.0246), and O^7–C^{35} 1.1435 Å (0.0287). The C–C bond lengths of C^{29}–C^{30} 1.4934 Å (0.0307), C^{35}–C^{36} 1.5152 Å (0.0350), C^5–C^6 1.4574 Å (0.0298), and C^{11}–C^{12} 1.4417 Å (0.0306) are shorter than a standard C–C single bond (1.53 Å) and longer than a double bond (1.32 Å). These structural features of complex **I** indicate that there is partial shift of electrons from ferrocene to C=O groups. In the compound **I** the carbonyl group contacts with CH_2 groups (C–H···O) next to the N atom are determined to be 2.429, 2.573, 2.429, and 2.573 Å. Overall the molecules form the clams-type structure with the phenyl ring orientated likes a cap above the heterocycle.

In the crystal structure of the compound **I** angles of the central tetrahedral N atom range from 114.90° (1.70) to 123.55° (1.86). These data are close to the

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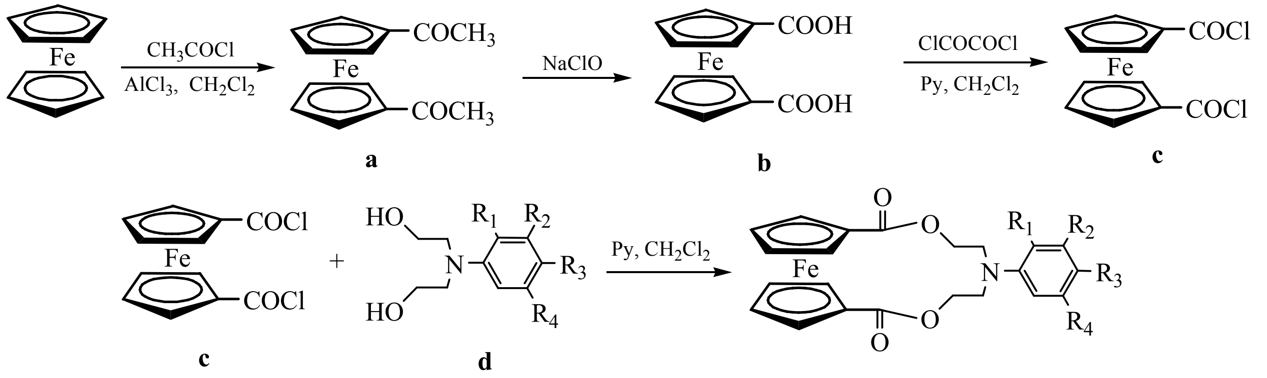
[1] The text was submitted by the authors in English.

Scheme 1.



I: $R^1 = H$, $R^2 = CH_3$, $R^3 = H$, $R^4 = CH_3$; **II:** $R^1 = H$, $R^2 = CH_3$, $R^3 = H$, $R^4 = H$; **III:** $R^1 = H$, $R^2 = Cl$, $R^3 = H$, $R^4 = H$; **IV:** $R^1 = CH_3$ $R^2 = H$, $R^3 = H$, $R^4 = H$; **V:** $R^1 = H$, $R^2 = Cl$, $R^3 = CH_3$, $R^4 = H$.

characteristics of a regular tetrahedron. The hydroxyl group H atom in compound **I** is engaged in intramolecular hydrogen bonding , such as weak C–H···O and C–H···C interactions (Fig. 2).

The aggregate is neither traditional J- nor H-type. Its molecular structure and 3-D framework indicate that the molecular plane is somewhat twisted due to the additional steric interactions caused by the C=O group and the intermolecular H-bonds (C–H···O, C–H···Π, C–H···N, C–H···H, and C–H···C) (Fig. 3).

The fluorescence intensity of compound **V** is the weakest and its emission wavelength is blue shifted. The electrophilic meta-Cl substituent makes a higher contribution into the effect than other substituents. The compounds **I–IV** exhibit similar spectral profiles with a weak peak at 334 nm and a strong one at 395 nm. In compound **I** the groups 3-CH_3, 5-CH_3, and benzenyl form the *p–π* conjugate system which enhances the fluorescence intensity. The strongest fluorescence intensity is registered for the compound **I**. The compound **II** exhibits stronger fluorescence intensity and a

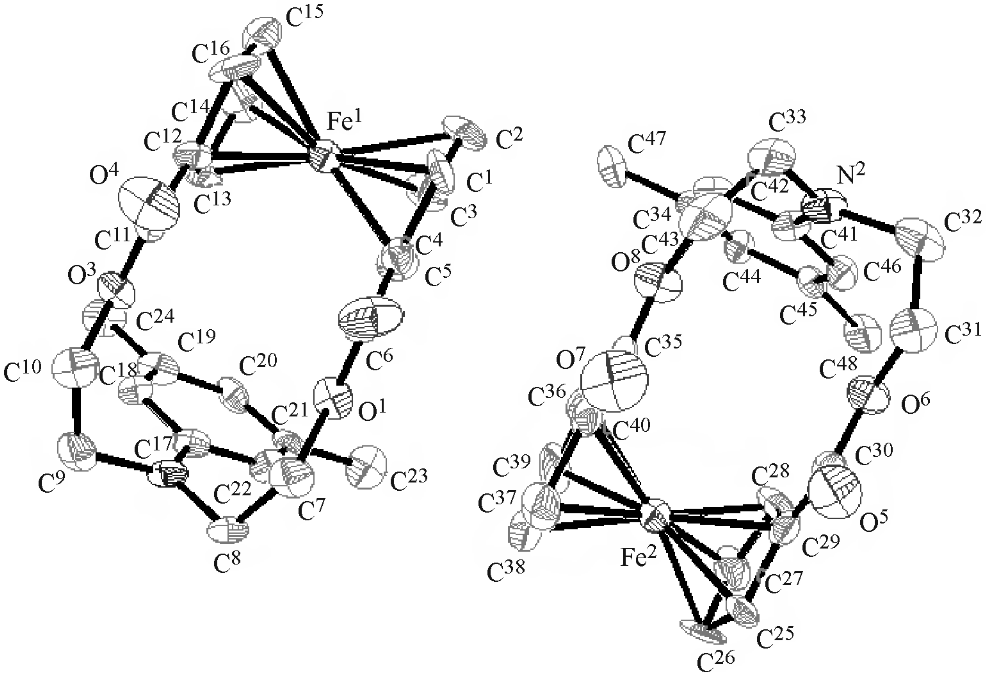


Fig. 1. Asymmetric unit of the compound **I** with thermal ellipsoids at the 50% probability level.

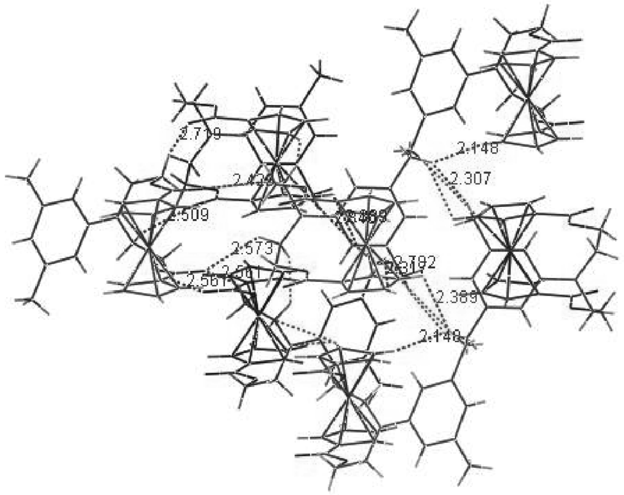


Fig. 2. Crystal structure of compound **I**: 3D short contacted network formed by the C–H···O, C–H···Π, C–H···N, C–H···H, and C–H···C interactions

smaller red shift than the compound **IV** which indicates that 2-CH_3 and 3-CH_3 on the benzenyl ring have different influence on fluorescence properties of the whole system.

Fluorescence of the compounds is consistent with their UV spectra. E2 band induced by π~π *transition of ferrocenyl and benzenyl fragments is registered at 228 nm. The absorption band at ca ~270–290 nm is induced by $n \rightarrow \pi^*$ transition. The red shift could be caused by the twisted intramolecular charge transfer (TICT). Luminescent compounds composed of complexes are of certain interest due to their potential applications as enzyme models and molecular recognition hosts. Therefore, in the present work, the luminescent properties of compounds were studied in the solid state at room temperature.

EXPERIMENTAL

Compound **I** was crystallized by slow diffusion of dichloromethane and ethyl acetate solutions to give red crystals that were studied by Bruker Smart-1000 CCD diffractometer with graphite monochromated MoK_α radiation. The data were collected at 293 K using the X-2H scan technique. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 970586.

Synthesis of ferrocenophanes esters *(general procedure).* 1,10-Ferrocene-di(carbonyl chloride) (1.0 g, 3 mmol) was added dropwise over 8 h to a mixture of the diols (3 mmol), dry DCM (800 mL), and 0.5 mL (6 mmol) of pyridine with stirring at room temperature. Stirring lasted for one day at room temperature followed by refluxing for 4 h (monitored by TLC). About 700mL of the solvent was evaporated and the residual solution was washed with 50 mL of water three times and dried over anhydrous $MgSO_4$. Upon filtration the solvent was removed to give a crude product. Column chromatography on silica gel (petroleum ether : ethyl acetate : dichloromethane 8 : 2 : 1) afforded ester ferrocenophane.

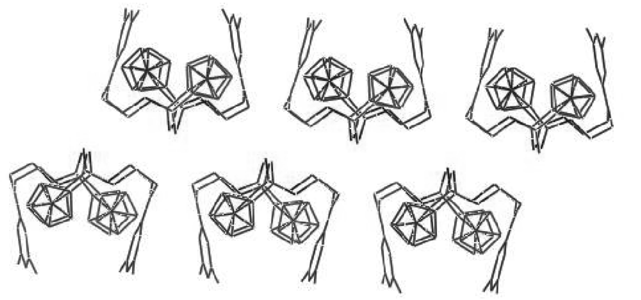


Fig. 3. Assembling of molecules of the compound **I** into a lot of “frog” 3D structure.

1,1'-Ferrocene-dicarboxyl-{[(3,5-dimethyl)phenyl)-imino]di-2,1-ethanediyl} (I). Red solid (55%), mp 158–159°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.49 m (1H, aromatic), 6.42 m (2H, aromatic), 4.70 m (4H, Fc-H), 4.50 t [4H, (–O–CH_2–)], 4.47 m (4H, Fc-H), 3.72 t [4H, (–N–CH_2–)], 2.29 s (6H, –CH_3–). IR spectrum (KBr), ν, cm^{-1}: 3408, 3096, 2920, 1735, 1698, 1592, 1465, 1385, 1283, 1209, 1154, 1050, 919, 810, 764, 682, 615, 545, 507, 485, 434. Calculated, %: C 64.44, H 5.63. $C_{24}H_{25}FeNO_4$. Found, %: C 64.01, H 5.10. MALDI-TOP MS $m/z = 448\ [M + H]^+$.

1,1'-Ferrocene-dicarboxyl-{[(3-methylphenyl)-imino]di-2,1-ethanediyl} (II). Red solid (45%), mp 165–166°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.17 m (1H, aromatic), 6.63 m (3H, aromatic), 4.70 m (4H, Fc-H), 4.50 t [4H, (–O–CH_2–)], 4.47 m (4H, Fc-H), 3.74 t [4H, (–N–CH_2–)], 2.34 s [3H, (–CH_3–)]. IR spectrum (KBr), ν, cm^{-1}: 3427, 3098, 2927, 1719, 1597, 1497, 1467, 1383, 1283, 1153, 1036, 921, 834, 766, 686, 597, 544, 506, 486, 435. Calculated, %: C 63.76, H 5.35. $C_{23}H_{23}FeNO_4$. Found, %: C 61.89, H 5.25. MALDI-TOP MS $m/z = 434\ [M + H]^+$.

1,1'-Ferrocene-dicarboxyl-{[(3-chlorophenyl)-imino]di-2,1-ethanediyl} (III). Yellow solid (38%), mp 245–246°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.80 m (2H, aromatic), 6.71 m (2H, aromatic), 4.68 m (4H, Fc-H), 4.49 t [4H, (–O–CH_2–)], 4.47 m (4H, Fc-H), 3.75 t [4H, (–N–CH_2–)]. IR spectrum (KBr), ν, cm^{-1}: 3434, 3102, 2926, 1730, 1590, 1555, 1464, 1386, 1282, 1152, 1032, 980, 916, 828, 757, 674, 597, 543, 484, 431. Calculated, %: C 58.24, H 4.44. $C_{22}H_{20}Cl·FeNO_4$. Found, %: C 58.95, H 4.54. MALDI-TOP MS $m/z = 454\ [M + H]^+$.

1,1'-Ferrocene-dicarboxyl-{[(2-methylphenyl)-imino]di-2,1-ethanediyl} (IV). Yellow solid (38%), mp 150–151°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.26 m (3H, aromatic), 7.09 m (1H, aromatic), 4.81 m (4H, Fc-H), 4.51 m (4H, Fc-H), 4.30 t [4H, (–O–CH_2–)], 3.41 t [4H, (–N–CH_2–)], 2.50 s [3H, (–CH_3–)]. IR spectrum (KBr), ν, cm^{-1}: 3430, 3100, 2922, 1723, 1626, 1578, 1461, 1374, 1279, 1147, 1027, 917, 825, 763, 730, 604, 535, 472. Calculated, %: C 63.76, H 5.35. $C_{23}H_{23}FeNO_4$. Found, %: C 61.89, H 5.25. MALDI-TOP MS $m/z = 434\ [M + H]^+$.

1,1'-Ferrocene-dicarboxyl-{[(3-chloro-4-methyl)-phenyl)imino]di-2,1-ethanediyl} (V). Yellow solid (30%), mp 163–164°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.09 m (1H, aromatic), 6.83 m (1H, aromatic), 6.65 m (1H, aromatic), 4.69 m (4H, Fc-H), 4.75 t [4H, (–O–CH_2–)], 4.72 m (4H, Fc-H), 3.68 t [4H, (–N–CH_2–)], 2.29 s [3H, (–CH_3–)]. IR spectrum (KBr), ν, cm^{-1}: 3433, 3102, 2924, 1728, 1612, 1551, 1507, 1464, 1386, 1283, 1150, 918, 826, 795, 767, 665, 576, 540, 540, 483. Calculated, %: C 59.06, H 4.74. $C_{23}H_{22}Cl·FeNO_4$. Found, %: C 57.45, H 4.68. MALDI-TOP MS $m/z = 468\ [M + H]^+$.

CONCLUSIONS

Five novel ferrocenyl heterocyclic compounds were synthesized in very dilute media and at low temperature to avoid polymerization. A crystal of ferrocenyl heterocyclic compound **I** was produced and studied. The novel compounds have a potential of receptors in cation or anion recognition.

ACKNOWLEDGMENTS

This work was supported by the Natural Science Foundation of China (grant no. 20972125) and by the Scientific Research Fund Project of the Yu-Lin University of Yulin (grant no. 14GK26).

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