



新型一维链状化合物 *N*-(*m*-二茂铁苯基)甲酰胺的合成及晶体结构

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Synthesis and Crystal Structure of a Novel One-Dimensional *N*-(*m*-Ferrocenylphenyl)-Formamide

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Abstract: *N*-(*m*-ferrocenylphenyl)-formamide has been synthesized by the reaction of *m*-ferrocenyl-aniline with DMF, and characterized by elements analysis, IR, ¹H NMR, and X-ray structure determination. The crystallized was in the monoclinic, *P*2₁/*c* space group, with *a*=0.140 94(3) nm, *b*=0.102 87(2) nm, *c*=0.100 26(2) nm, β =104.85(3) $^\circ$ and final *R* indices [*I*>2 σ (*I*)] *R*₁=0.072 7, *wR*₂=0.184 5. An infinite one-dimensional chain is formed by inter-molecular hydrogen bonding N—H \cdots O. Cyclic voltammetry was studied comparing with the parent compound (*m*-ferrocenylaniline). CCDC: 243511.

Key words: ferrocene; crystal structure; hydrogen bond; cyclic voltammetry

0 Introduction

Ferrocene derivatives are attracting much attention from the viewpoint of catalysis, organic synthesis and functional materials and electronchemistry^[1]. Special interest is the redox chemistry of the iron center and the structure^[2], in redox system, ferrocene could act as a reversible one-electron redox nucleus. The electronic properties that may result in novel functions and applications are related to π -conjugated organic polymers^[3]. It was reported that ferrocenylphenyl group is an excellent electron transfer mediator^[4], and could be used to evaluate the effect of the extended π interaction in the ligand and lowered symmetry of the molecules on the ion states^[5]. Formamides are a class

of important intermediates in organic synthesis and widely used to catalyze reactions such as allylation and hydrosilylation of carbonyl compounds^[6]. They are very useful reagents in Vilsmeier formylation reactions too^[7], and chiral formamides were found to be one of the best candidates for the asymmetric allylation^[8]. Incorporation of a ferrocene moiety into an organic molecule of formamides could impart the chemical and physicochemical properties that are absent or little manifested in the parents substance^[9]. We are interested in functionalized ferrocene derivatives, which could potentially serve as efficient mediators for biosensors and new bioorganometallic mediators^[4]. In this paper we report the synthesis of *N*-(*m*-ferrocenylphenyl)-formamide and present its results of

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electrochemical and thermogravimetric studies. The crystal structure of the title compound is also presented.

1 Experimental

1.1 Materials and instruments

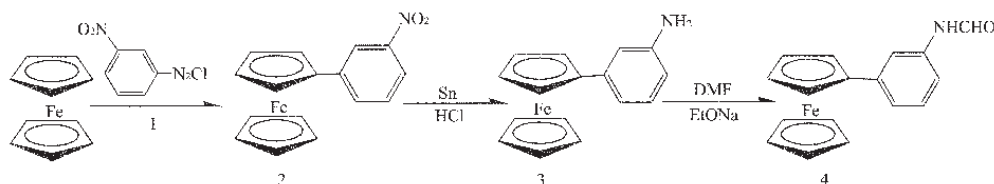
IR spectra were recorded on a Bruker-VECTOR22 spectrophotometer as KBr pellets in the 400~4 000 cm^{-1} regions. ^1H NMR spectra were recorded on a Bruker-DPX400 spectrometer, using CDCl_3 as solvent and tetramethylsilane as an internal standard. Elemental analyses were determined with a Carlo Erba 1106 elemental analyzer. The melting point was mea-

sured on a X4 instrument and uncorrected. Electrochemical experiments were performed using CHI 650A electrochemical workstation. All chemicals were reagent grade quality obtained from commercial sources, and solvents were purified by standard method.

1.2 Synthesis

Diazotization of *m*-nitro-benzene **1**, *m*-ferrocenyl-nitrobenzene **2**, *m*-ferrocenylaniline **3** were prepared according to literature^[10].

General procedure for synthesis of the title compound (**4**) is shown in scheme 1.



Scheme 1

Na (0.025 mol) was added to 15 mL absolute ethanol solution, the mixture was refluxed with stirring for 2 h. The mixture was cooled to room temperature and DMF (1.5 mL) was added. Then *m*-ferrocenylaniline (0.010 mol) in absolute ethanol was dropped. After stirring for 3 h under nitrogen atmosphere, the solvent was evaporated under vacuum to dryness and then purified by a column of silica gel with dichloromethane: petroleum ether (1:1) as eluent, a yellow solid was obtained, yield: 20%, m.p.: 144~145 $^{\circ}\text{C}$. IR (KBr, cm^{-1}): 3 421(-NH), 1 671 (-C=O), 1 610, 1 500 (-ph), 1 104 and 1 004 (Fc), 1 304 (Ar-N). ^1H NMR (DMSO, δ ppm): 4.04(s, 5H, -Fc), 4.33(d, $J=1.41\text{Hz}$, 2H, -Fc), 4.58(d, $J=1.612$, 2H, -Fc), 6.5(d, $J=7.52\text{Hz}$, 1H, H-Ar), 6.81(s, 1H, H-Ar), 6.9(d, $J=7.59\text{Hz}$, 1H, H-Ar), 7.0(t, $J=7.70\text{Hz}$, 1H, H-Ar), Anal. Calc. for $\text{C}_{17}\text{H}_{15}\text{FeNO}$ (%): C 66.91; H 4.95; N 4.59. Found (%): C 66.75; H 5.05; N 4.47.

Single crystals of compound **4** suitable for X-ray analysis were obtained in mixture of dichloromethane and petroleum ether at room temperature.

2 X-ray crystallography

A yellow color crystal with dimensions of 0.30 mm \times 0.20 mm \times 0.20 mm is mounted on a glass fiber. All data are collected on a Rigaku-Raxis-IV area detector, equipped with graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.071\,073\text{ nm}$) at 291 K. A total

of 3 885 reflections are collected, of which 2 191 are unique reflections. The data are corrected for Lorentz and polarization effects. The structure is resolved by direct methods and expanded with difference Fourier synthesis. All non-hydrogen atoms are subjected to refine anisotropically. Hydrogen atoms are included but not refined. The final refinement by full-matrix least-squares is converged to $R=0.072\,7$ and $wR=0.184\,5$, $(\Delta\rho)_{\text{max}}=1.317\text{ e}\cdot\text{nm}^{-3}$, $(\Delta\rho)_{\text{min}}=-565\text{ e}\cdot\text{nm}^{-3}$. The compound belongs to monoclinic system, $P2_1/c$ space group, with $a=1.409\,4(3)\text{ nm}$, $b=1.028\,7(2)\text{ nm}$, $c=1.002\,6(2)\text{ nm}$, $\beta=104.85(3)^{\circ}$, $V=1.405\,1(5)\text{ nm}^3$, $Z=4$, $D_c=1.443\text{ Mg}\cdot\text{m}^{-3}$, $\mu=1.067\text{ mm}^{-1}$, $F(000)=632$. All calculations were performed with the SHELX-97 crystallographic software package^[11].

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The crystal structure of *N*-(*m*-ferrocenylphenyl)-formamide is shown in Fig.1. The cyclopentadienyl rings in ferrocenyl fragment are planar and nearly parallel with a dihedral angle of 1.7° . Fe-C_{ring} distances range from 0.201 0(7) nm to 0.205 0(7) nm and intracyclopentadienyl C-C bond lengths lie in the range from 0.135(2) nm to 0.144 4(12) nm, C-C-C angles (average $108.0(5)^{\circ}$) are all similar to those reported in the literature^[12]. The bond lengths and angles within the phenyl group are unexceptional. It is clear from the structure that the phenyl ring is almost coplanar to the cyclopentadienyl ring plane to which it

is attached, their dihedral angle (planes C11-C16 and C6-C10) is 4.3° . The bond distance of O1-C17 is 0.122 4(8) nm, which is consistent with the distance of C=O.

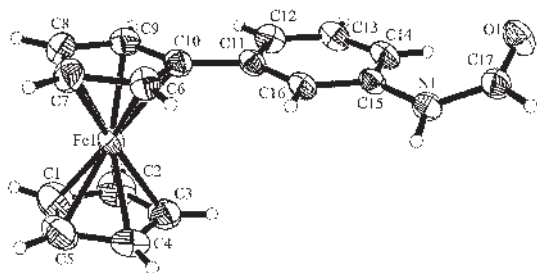


Fig.1 Molecular structure of *N*-(*m*-ferrocenylphenyl)-formamide

In the packing diagram (Fig.2), the compound is connected to each other by intermolecular hydrogen bond N—H \cdots O, forming a one-dimensional chain structure. The hydrogen bond originates from NH of one compound with O of neighboring compound [O1 \cdots N1=2.910, H1 \cdots O1=0.206 7 nm, N1—H1 \cdots O1=

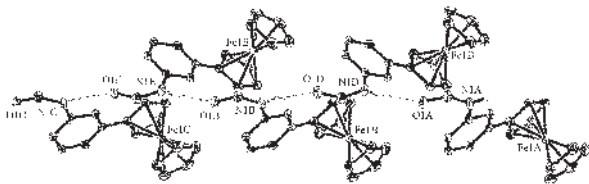


Fig.2 Packing diagram of the title compound

Table 1 Crystal data and structure refinement for compound 4

Empirical formula	C ₁₇ H ₁₅ FeNO
Formula weight	305.15
Calculated density / (Mg·m ⁻³)	1.443
Absorption coefficient / mm ⁻¹	1.067
<i>F</i> (000)	632
Crystal size / mm	0.30 × 0.20 × 0.20
θ range for data collection / (°)	1.49 to 25.00
Index ranges	$-16 \leq h \leq 16$, $-12 \leq k \leq 12$, $0 \leq l \leq 11$
Reflections collected / unique	3 885 / 2191 [<i>R</i> (int)=0.037 8]
Max. and min. transmission	0.815 0 and 0.740 3
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	2 670 / 0 / 182
Goodness-of-fit on <i>F</i> ²	1.129
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.0727, 0.1845
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0861, 0.1894

166.74°]. Obviously, the N—H \cdots O interactions are strong. The crystal data and selected bond lengths and angles are given in Table 1 and Table 2.

Table 2 Bond lengths (nm) and angles (°) for the compound

N(1)-C(17)	0.133 5(8)	C(16)-C(15)-N(1)	117.9(6)
N(1)-C(15)	0.142 4(8)	C(14)-C(15)-N(1)	121.6(6)
O(1)-C(17)	0.122 4(8)	C(6)-C(10)-C(11)	126.8(6)
C(10)-C(11)	0.147 9(9)	O(1)-C(17)-N(1)	126.5(7)
		C(17)-N(1)-C(15)	126.6(5)

3 Electrochemistry

Electrochemical experiments were performed in dry acetonitrile using CHI 650A electrochemical workstation. A three-electrode configuration was used. The working electrode was a GC disk (diameter 3.0 mm). The reference electrode was a saturated calomel electrode (SCE), and the auxiliary electrode was a platinum wire. The experiments were carried out under a moisture free N₂ atmosphere using (*n*-Bu)₄NClO₄ (TBAP) as the supporting electrolyte.

First we present the investigation by cyclic voltammetry of the behaviour of compound 4 in concentrations of 0.5~1 mmol·dm⁻³ in acetonitrile, using 0.1 mol·dm⁻³ TBAP as supporting electrolyte. One pair of well-defined and stable redox waves for substituted ferrocene derivatives in solution is observed (Fig.3a). The formal potential value taken as an average of anodic and cathodic peak potentials is $E^{\ominus}=510$ mV (vs SCE) for compound 4. The value of E^{\ominus} is difference to that of *m*-FcC₆H₄NH₂ ($E^{\ominus}=375$ mV, $\Delta E_p=135$ mV) suggesting that the electron withdrawing alcohol group in compound 4 significantly influence the redox potential of the iron center.

Electrochemical reversibility is judged on the basis of ΔE_p separation and also on the ratio of anodic to cathodic peak currents. For compound 4 ΔE_p separation values of 70~80 mV in the 50~500 mV·s⁻¹ range of scan rate, are measured in agreement both with theoretical value for a one-electron Nernst system in the absence of *iR* drop^[13] and with the previously obtained values for simple ferrocene or ferrocene derivatives^[14,15]. It is thus confirmed that the ferrocene group undergoes a one-electron oxidation/reduction. An analysis of the CVs, varying both scans rate (*v*) and concentration (*c*) between 0.5 and 1 mmol·dm⁻³, has

shown symmetrical redox waves. In addition it is found that i_p is linearly proportional to $v^{1/2}$ (Fig.3b), confirming the reversible diffusion-controlled process for the Fc^+/Fc electrochemical system. This is also judged from chronoamperometric experiments. The diffusion coefficient of compound **4** is computed using CV and Cottrell relationships. The resulting values for the diffusion coefficient obtained by these two methods are $1.45 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ and $1.33 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ respectively, the average is $1.39 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$, that is quite close to the previous data reported of ferrocene or ferrocene derivatives^[16,17].

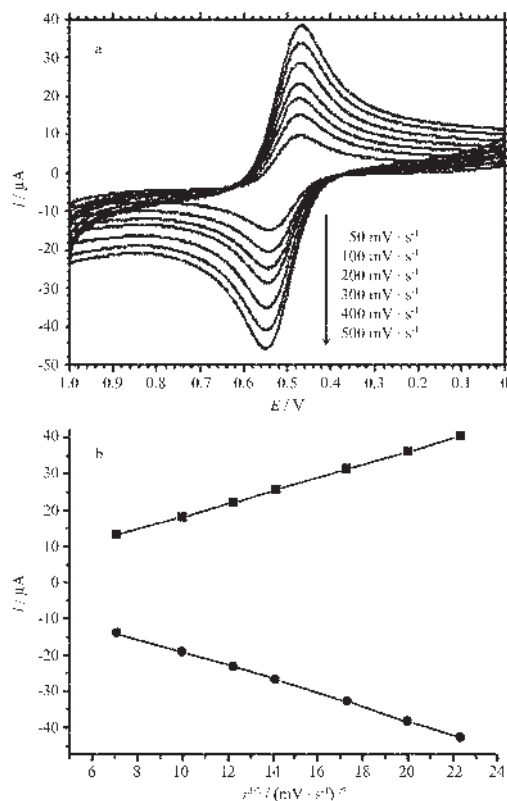


Fig.3 (a) Cyclic voltammograms of compound **4** in acetonitrile at different scan rate, (b) Linear relation between the peak current and the square root of the scan rate
Working electrode: 3 mm diameter glassy carbon disc. Reference electrode: SCE.
Supporting electrolyte: 0.1 mol·dm⁻³, TBAP.
 $c_{\text{Fc}} = 1 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$.

4 Thermogravimetric analysis (TGA)

TGA-DTA measurement is performed by heating the sample from 20 °C to 1 000 °C at a rate of 15 °C·min⁻¹ in air on a Perkin-Elmer DTA-7 and TGA-7 differential thermal analyzer.

The TG-DTA of compound **4** is determined in the range of 20~1 000 °C in the air. The TG curve exhibits three continuous weight loss stages in the ranges 36~70, 135~261, 298~460 °C, corresponding to the concomitant release of the solvent, decomposition phenyl-formamide and ferrocene. Finally, a plateau region is observed from 460~1 000 °C. A brown dark residue of Fe_2O_3 is remained. There are one strong endothermic peak (134.5 °C) and one strong exothermic peak (460~550 °C) in DTA curve.

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