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Synthesis, Structure and Properties of a Novel Cu(II) Complex Constructed from Designed Ferrocenyl Ligand

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The treatment of $Cu(NO_3)_2 \cdot 3H_2O$ with 3-carboxymethylamino-1-ferrocenyl-2-buten-1-one ($FcC(O)CH{=}C(CH_3)NHCH_2COOH$) in the presence of 1,10-phenantholine (phen) in methanol solution resulted in a novel complex $[Cu(\eta^3\text{-}FcC(O)CH{=}C(CH_3)NCH_2COO)(phen)]\cdot 1.5H_2O$ (1). The molecular structure of complex 1 has been characterized by elemental analysis, IR and single crystal X-ray diffraction. Its thermal and electrochemical properties are presented.

Keywords copper(II) complex, structure, designed ferrocenyl ligand, thermal and electrochemical properties

INTRODUCTION

Ferrocenyl complexes have attracted continuously much interest in the field of coordination chemistry due to their potential applications such as nonlinear optical materials, magnetic materials and catalysis and so on.[1–5] Therefore the design of various ferrocenyl ligands to build up desired complexes is very important. Up to date, two kinds of ferrocenyl compounds—ferrocene-substituted carboxylate[6–11] and pyridine-containing ferrocene[12–15] have mainly been used to construct novel complexes bearing ferrocene group. Recently, ferrocene-containing enaminones have also been explored in this context,[16–18] but the reported complexes with ferrocenyl enaminones are scarce.[19] Herein, we selected one novel ferrocenyl enaminone-based carboxylate compound, 3-carboxymethylamino-1-ferrocenyl-2-buten-1-one ($FcC(O)CH{=}C(CH_3)NHCH_2COOH$), and surmised that having both enaminone and carboxylate groups within the same ligand might generate interesting structures. To our knowledge so far, no article on crystalline complex constructed from organometallic enaminone-based carboxylate ligand has appeared, and in this paper we report the synthesis, crystal structure, thermal and electrochemical properties of the copper complex $[Cu(\eta^3\text{-}FcC(O)CH{=}C(CH_3)NCH_2COO)(phen)]\cdot 1.5H_2O$ (**1**).

EXPERIMENTAL

General Procedures

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. Ligand $FcC(O)CH{=}C(CH_3)NHCH_2COOH$ was prepared according to the literature methods.[19] Its sodium salt was prepared by reaction with sodium methoxide.

IR spectra were recorded on a Nicolet NEXUS 470-FTIR spectrophotometer as KBr pellets in the 400–4000 cm^{-1} region. Elemental analyses (C, H and N) were carried out on a FLASH EA1112 elemental analyzer. TG-DSC measurements were performed by heating the sample from 20°C to 650°C at a rate of $10°C/min^{-1}$ in air on a NETZSCH STA 409PC differential thermal analyzer. Cyclic voltammetry studies were recorded with an CHI650 electrochemical analyzer utilizing the three-electrode configuration of a Pt working electrode, a Pt auxiliary electrode, and a commercially available saturated calomel electrode as the reference electrode with a pure N_2 gas inlet and outlet. The measurements were performed in DMF solution containing tetraethyl ammonium perchlorate ($n\text{-}Bu_4NClO_4$) ($0.1\ mol \cdot dm^{-3}$) as supporting electrolyte, which has a 50 ms pulse width and a 20 ms sample width. The potential was scanned from +0.0 to +1.2 V at scan rate of 30 mV s^{-1}.

Caution ! Although no problems were encountered in this work, the salt perchlorates are potentially explosive. They should be prepared in small quantities and handled with care.

Preparation of $[Cu(\eta^3\text{-}FcC(O)CH{=}C(CH_3)NCH_2COO)(phen)]\cdot 1.5H_2O$ (1)

$FcC(O)CH{=}C(CH_3)NHCH_2COONa$ (16.4 mg, 0.05 mmol) in 3 mL of methanol solution was added dropwise to the solution of 3 mL of methanol of $Cu(NO_3)_2{\cdot}3H_2O$ (12.1 mg, 0.05 mmol). Then 2 mL of methanol of phen (10 mg, 0.05 mmol) was added slowly to the former mixture. The dark brown resulting mixed solution was stirred uniformly; subsequently the filtrate was allowed to stand at room temperature in the dark. Good quality blue-green crystals of $[Cu(\eta^3\text{-}FcC(O)CH{=}C(CH_3)NCH_2COO)(phen)]{\cdot}1.5H_2O$ (**1**)

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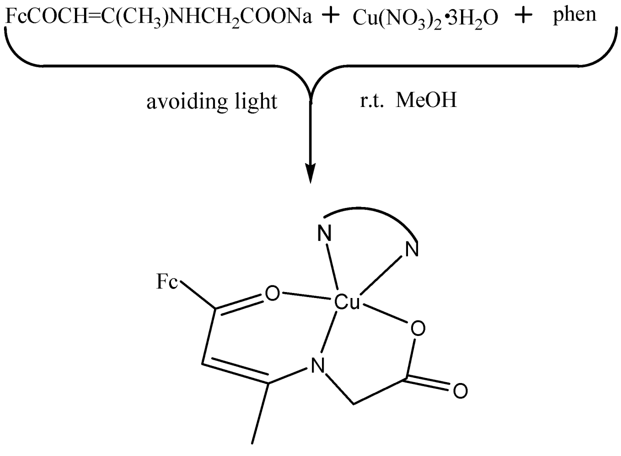
TABLE 1
Crystallographic data for **1**

Compound	1
Formula	$C_{28}H_{26}CuFeN_3O_{4.5}$
Fw	595.91
Crystal syst	Triclinic
Space group	P-1
Crystal size (mm)	0.20 × 0.18 × 0.17
a (Å)	10.722(2)
b (Å)	11.043(2)
c (Å)	12.180(2)
α (deg)	70.91(3)
β (deg)	82.18(3)
γ (deg)	83.27(3)
V (Å^3)	1346.1(5)
Z	2
Dc (mg m^{-3})	1.470
F(000)	612
μ (mm^{-1})	1.369
Theta range for data collection	1.78 to 25.50
Limiting indices	−12<=h<=12, −13<=k<=0, −14<=l<=13
Reflections collected/unique	4504/4504 [R(int) = 0.0000]
Max. and min. transmission	0.8006 and 0.7714
Data/restraints/parameters	4504/6/357
Goodness-of-fit on F^2	1.084
Final R indices [I>2sigma(I)]	R1 = 0.0621, wR2 = 0.1627
R indices (all data)	R1 = 0.0780, wR2 = 0.1759
$\Delta\rho_{max}$ and $\Delta\ \rho_{min}$ (e Å^{-3})	0.862 and −0.486

were obtained after two days. Yield: 78%. Anal. calcd. for $C_{28}H_{26}N_3O_{4.5}FeCu$: C, 56.43; H, 4.40; N, 7.05%. Found: C, 56.31; H, 4.52; N, 7.01%. IR (cm^{-1}, KBr): 3431s, 3092m, 1612s, 1505s, 1430s, 1386w, 1308m, 1286w, 1235w, 1142w, 1104m, 932w, 848m, 811w, 776w, 730m, 640w, 585w, 482w.

X-ray Crystallography

Crystal data and experimental details for compound **1** are contained in Table 1. All measurements were made on a Bruker Smart 1000 diffractometer with a graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). Red prismatic single crystal of (0.20 × 0.18 × 0.17 mm) was selected and mounted on a glass fiber. All data were collected at a temperature of 291(2) K using the ω -2θ scan technique and corrected for Lorenz-polarization effects. A correction for secondary extinction was applied. The structure was solved by direct methods and expanded using the Fourier technique. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included but not refined. The final cycle of full-matrix least squares refinement was based on 4504 observed reflections and 357 variable parameters. All calculations were performed using the SHELX-97 crystallographic software package.[20] The crystal data are deposited at Cambridge Crystallographic Data Centre, CCDC 693234.



Complex **1**

SCH. 1. [Fc= (η^5-C_5H_5)Fe(C_5H_4 − η^4); NN=phen].

RESULTS AND DISCUSSION

Synthesis

The blue-green crystalline complex **1** was prepared in good yield, as summarized in Scheme 1. The key of synthesis of the complex **1** is the avoidance of light, as noted in earlier studies.[10,14] The air-stable compound **1** was characterized by satisfactory C, H and N microanalysis, IR spectra, and finally by single crystal X-ray diffraction. The compound was insoluble in non-polar solvents such as in MeOH, EtOH or MeCN, but it was soluble in the highly polar solvents as DMSO or DMF.

The Molecular Structure of Crystalline Complex 1

The molecular structure of the crystalline compound **1** is shown in Figure 1; selected geometrical parameters are listed in Table 2.

TABLE 2
Bond lengths (Å) and bond angle (deg) of complex **1**

Cu(1)-O(1)	1.905(4)	Cu(1)-N(1)	1.920(4)
Cu(1)-O(2)	1.982(4)	Cu(1)-N(3)	2.040(5)
Cu(1)-N(2)	2.277(4)	N(1)-C(13)	1.306(6)
O(1)-C(11)	1.291(6)	N(1)-C(15)	1.464(7)
O(2)-C(16)	1.269(7)	O(3)-C(16)	1.243(7)
C(10)-C(11)	1.478(7)	C(11)-C(12)	1.386(7)
C(12)-C(13)	1.420(7)	N(1)-Cu(1)-O(2)	83.31(17)
N(3)-Cu(1)-N(2)	77.39(17)	O(1)-Cu(1)-N(1)	94.80(17)
O(1)-Cu(1)-O(2)	165.71(16)	N(1)-Cu(1)-N(3)	171.32(18)
O(1)-Cu(1)-N(3)	89.82(17)	O(1)-Cu(1)-N(2)	99.60(16)
O(2)-Cu(1)-N(3)	90.40(18)	O(2)-Cu(1)-N(2)	94.39(17)
N(1)-Cu(1)-N(2)	108.95(17)	C(11)-C(12)-C(13)	126.8(5)
C(13)-N(1)-C(15)	121.1(4)	C(13)-N(1)-Cu(1)	126.3(3)
C(15)-N(1)-Cu(1)	112.4(3)	O(1)-C(11)-C(12)	125.2(5)
O(1)-C(11)-C(10)	115.0(4)	C(12)-C(11)-C(10)	119.7(4)
N(1)-C(13)-C(12)	121.5(4)	C(12)-C(13)-C(14)	117.5(4)

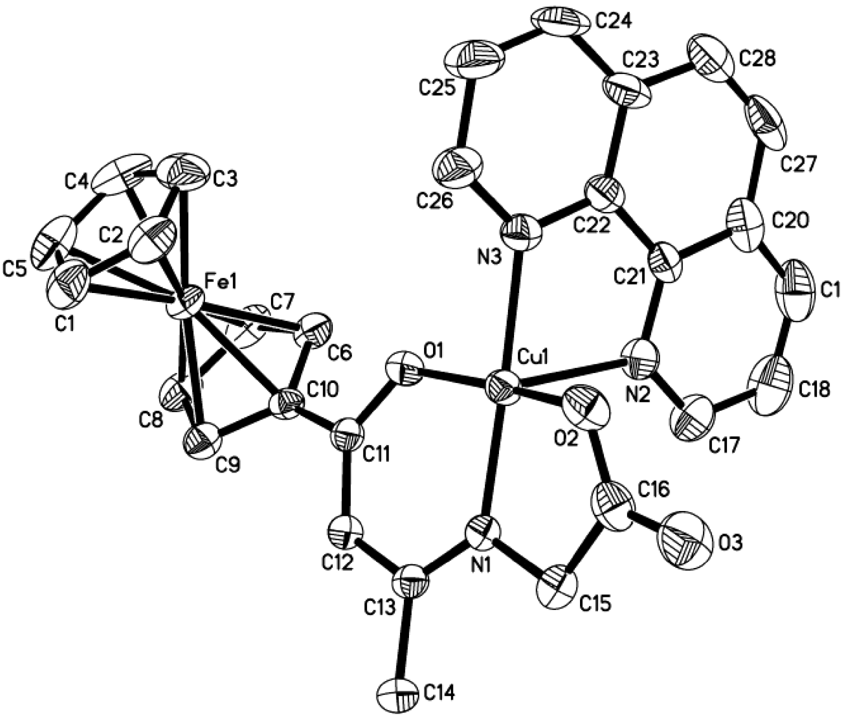


FIG. 1. The molecular structure of complex **1** (H atoms and solvent molecule omitted for clarity).

Single-crystal X-ray diffraction measurement shows that the crystal structure of the complex can be viewed as made up of [Cu(η^3-FcC(O)CH$_2$—C(CH$_3$)NCH$_2$COO)(phen)] unit and non-coordinated water molecules. The five-coordinate copper(II) atom displays a slightly distorted square-pyramidal geometry surrounded by two nitrogen atoms N2 and N3 from phen and three atoms, O1, N1 and O2 from one deprotonated ligand [η^3-FcC(O)CH$_2$ =C(CH$_3$)NCH$_2$COO]$^{2-}$. The plane (I) is defined by the four atoms N1, N3, O1 and O2 (the mean deviation from the plane is 0.0627 Å), while Cu1 is located above the plane (distance from the center of the plane being 0.191 Å). The in-plane Cu1-N bond lengths are within the range 1.920–2.040 Å. The in-plane Cu1-O1 and Cu1-O2 distances are 1.905 Å and 1.982 Å, respectively. The axial bond distance of Cu1-N2 is 2.277 Å, which is significantly longer than the bond distances in the plane I. This interesting feature is unexpected, because

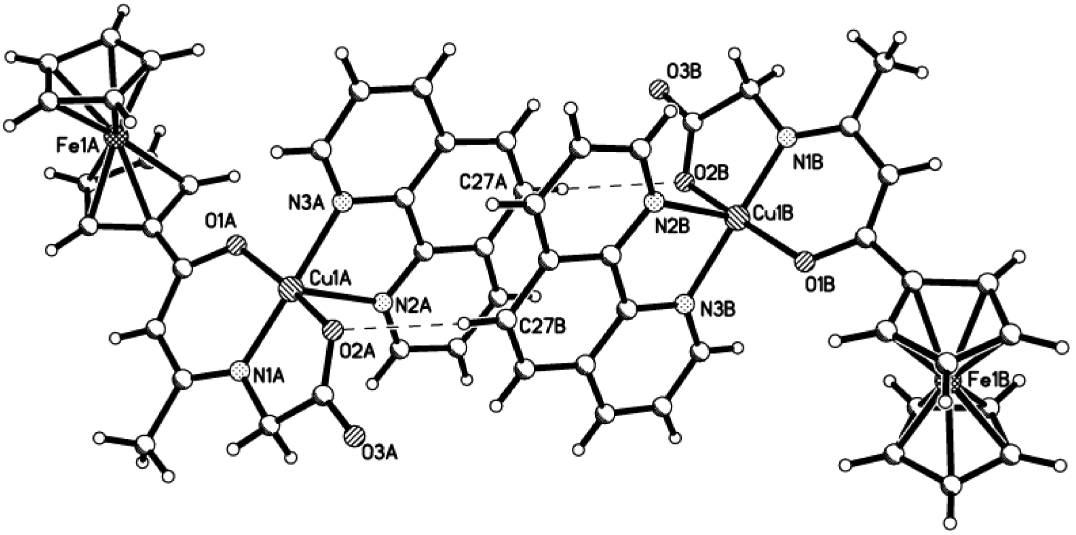


FIG. 2. The dimeric unit of complex **1** supported by weak hydrogen-bonding and strong $\pi - \pi$ stacking.

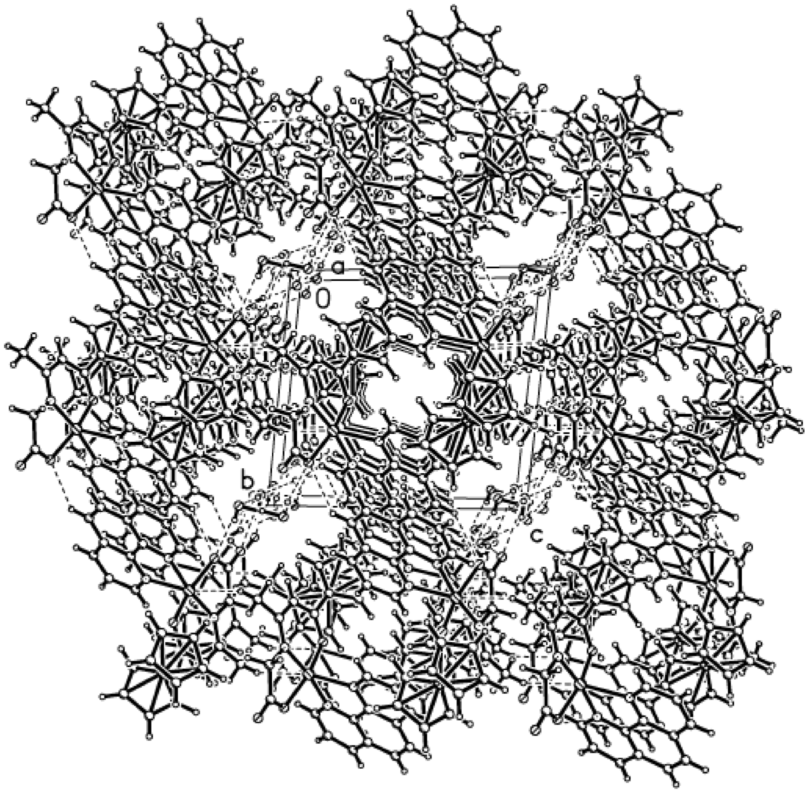


FIG. 3. Crystal packing of complex **1** in the solid.

the axial bond in square-pyramidal Cu(II) is usually long and varies between 2.12 and 2.6 Å for O or N coordination, due to Jahn-Teller effects.[21] It is to be pointed out that the O1-C11, C11-C12, C12-C13 and C13-N1 bond distances are of 1.296, 1.386, 1.420 and 1.306 Å, respectively. These suggest that the O=C—C=C—N system of the complex has more delocalization than that of the corresponding ligand.[19]

Interestingly, it can be seen from Figure 2, the phen rings of neighboring [Cu(η^3-FcC(O)CH_2 =C(CH_3)NCH_2COO)(phen)] units are face-to-face arranged, while the distance between the two rings is 4.210 Å and dihedral angle is 0° indicating the existence of $\pi - \pi$ stacking interactions. Additionally, there are weak C—H · · · O hydrogen bonds between the neighboring units, which originate from CH of one [Cu(η^3-FcC(O)CH_2=C(CH_3)NCH_2COO)(phen)] unit with O from the carbonyl group of neighboring [Cu(η^3-FcC(O)CH_2=C (CH_3)NCH_2COO)(phen)] unit. Thus, the dimeric Cu(II) unit was built up.

Within the ferrocene fragments, the C—C distances, Fe–C_{ring} distances and C—C—C angles are all similar to those reported in the literature.[8] The cyclopentadienyl rings are planar and parallel with a dihedral angle of 3.8°. The bond lengths and

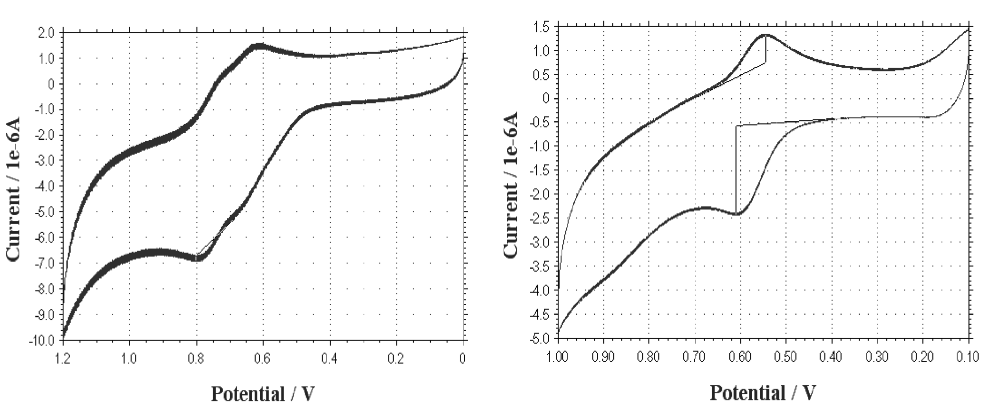


FIG. 4. Cyclic voltammogram of complex **1** (right) and the corresponding ferrocenyl ligand, 3-carboxymethylamino-1-ferrocenyl-2-buten-1-one (left) (~1.0 × 10^{-3} M) in DMF containing n-Bu_4NClO_4 (0.1 M) at a scanning rate of 30 mV s^{-1} (vs. SCE).

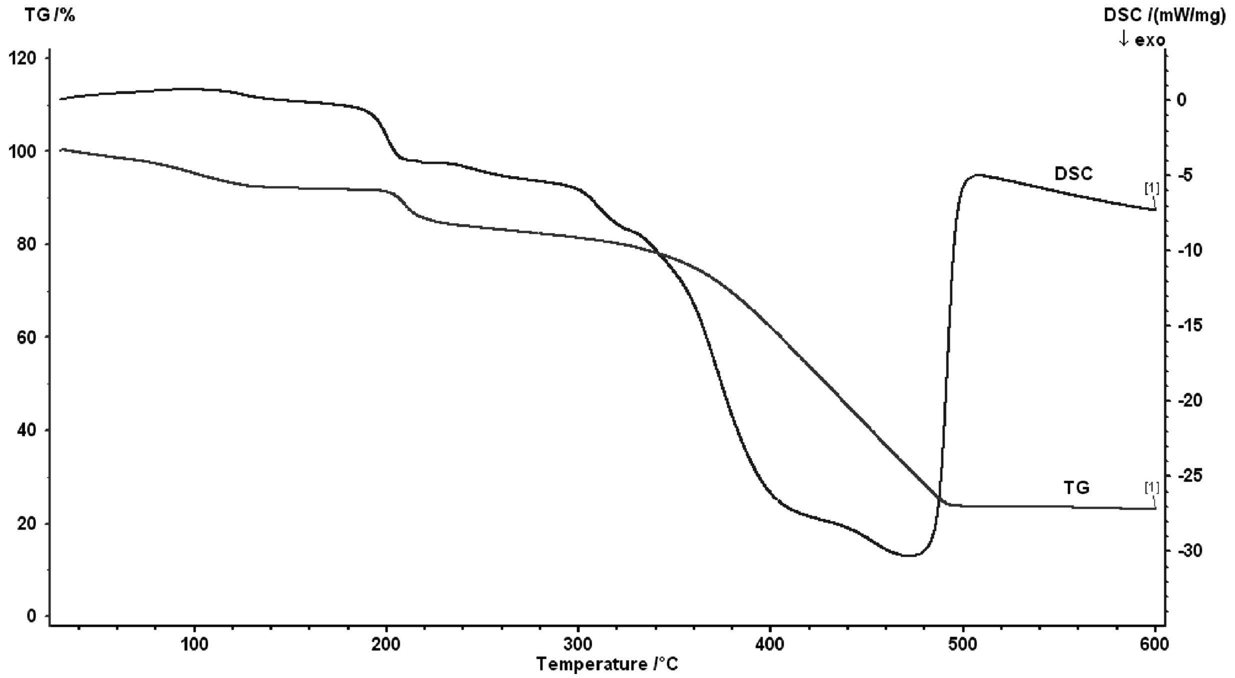


FIG. 5. Thermogravimetric curve of complex **1**.

angles within the phen ligand are also unexceptional and close to those reported in the literature.

In addition, in the solid-state, a large number of crystallization water molecules can form hydrogen bonds with the surrounding units. Therefore a stable three-dimensional solid-state structure is constituted (Figure 3).

IR Spectroscopy

According to the references,[9,10] the characteristic IR bands of the ferrocenyl group at 3097 and 489 cm^{-1} due to ν(C—H) and ν (Fe-Cp) vibrations, respectively, which can be found in the compound (3092 and 482 cm^{-1}). The bands attributable to H_2O occur at position of 3431 cm^{-1}. The strong absorption bands at 1612 and 1505 cm^{-1} are assigned to $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ vibrations, respectively, and the vibrational bands around 1308 and 1104 cm^{-1} can be attributed to the $\delta(CH_3)$ and $\rho(CH_3)$, respectively.[22] The characteristic absorption of phen are observed as four strong or medium bands in 1533, 848, 776 and 730 cm^{-1}. In conclusion, these IR data are consistent with the crystal data of the compound **1**.

Electrochemical Studies of Complex 1

As can be see from Figure 4, both the complex and corresponding ferrocenyl ligand exhibit a quasi-reversible oxidation-reduction process, which can be assigned to the oxidation of the ferrocene unit. The oxidation and reduction peaks of the ligand 3-carboxymethylamino-1-ferrocenyl-2-buten-1-one are 0.803 V and 0.752 V, respectively, and the electric potential difference of both peaks is 0.051 V. Oxidation and reduction peaks of the complex are 0.611 V and 0.545 V, respectively, and the electric potential difference of both peaks is 0.066 V. Obviously, Cu(II) ion has a significant effect to oxidation-reduction potentials of the ferrocenyl group in the complex. Thus, both oxidation and reduction electric potentials have a marked shift to the lower potential. The migration rates of one oxidation peak (0.192 V) and of the reduction peak (0.207 V) are very close, which resulted in the slight change of the electric potential difference.

Thermogravimetric Analysis (TGA)

The TG-DSC measurements of complex **1** were determined in the range of 20–650°C in air. TG data (Figure 5) shows that complex **1** is stable up to 67.4°C, then firstly loses weight from 67.4 to 130°C corresponding to losses of the uncoordinated water molecules, secondly goes through complicated multiple weight loss steps in the temperature range of 130–500°C corresponding to the decomposition of phen and the organic units of ferrocenyl ligand. Finally, a plateau region is observed from 500 to 650°C. A dark-brown amorphous residue of FeO+ CuO (observed 25.16%, calculated 25.51%) remained. There is one very strong exothermic peak (395.6°C) on the DSC curve of **1**.

Supplementary Material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 693234. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: + 44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or kwww:http://www.ccdc.cam.ac.ukl).

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Illustrations

Synthesis, structure and properties of a novel Cu(II) complex constructed from designed ferrocenyl ligand

One novel complex $[Cu(\eta^3\text{-FcC(O)CH=C(CH}_3\text{)NCH}_2\text{COO)(phen)}]\cdot 1.5H_2O$ has been prepared and structurally characterized. There are three kinds of components in the complex, copper ions, ferrocenyl enaminone-based carboxylate units and 1,10-phenantholine. The molecular structure of the complex has been characterized by elemental analysis, IR and single crystal X-ray diffraction. Its thermal and electrochemical properties are presented.