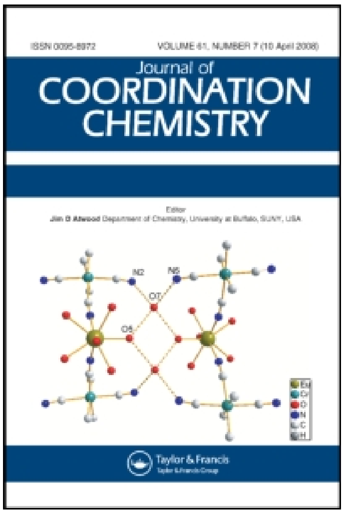

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Syntheses and crystal structures of transition metal complexes of 1,1'-bisacetylacetoferrocene

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Syntheses and crystal structures of transition metal complexes of 1,1′-bisacetylacetoferrocene

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Bimetallic complexes **3a**–**e** of 1,1′-bisacetylacetoferrocene (**2**) were prepared by reactions of transition metal acetates $M(OAc)_2$ ($M = Co^{2+}$, Mn^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}) with the **2** in refluxing methanol. The X-ray structures of the cobalt and manganese complexes were determined showing very similar centrosymmetric macrocyclic dimeric frameworks constituted by linkage of two Co^{2+} or Mn^{2+} ions and two 1,1′-diacetoacetylferrocene units with two additional methanols as bridges dividing this macrocyclic framework into two small cyclic subunits. The UV-Vis spectra and electronic properties were also studied.

Keywords: Ferrocene; Acetylacetone; Transition metal complexes; Electrochemistry

1. Introduction

Ferrocene and its derivatives are well known for novel function and versatile application in a wide range of fields [1]. Coordination complexes of transition metal ions containing ferrocene moieties have been investigated intensively in recent years for redox active centers, nonlinear optical properties, interesting electronic and medical applications [2, 3]. As one kind of potentially valuable ligand, ferrocene-containing β-diketones $FcCOCH_2COR$ were synthesized and used to prepare a number of transition metal complexes. In these studies attention was given to the mono-β-diketone functional group on the ferrocene ring with R being alkyl, aryl or trifluoromethyl groups etc. [4–8]. The investigation of ferrocene-containing bis-β-diketone as chelates has attracted less attention [9, 10]. By using ferrocene-containing bis-β-diketone as starting material Tarrago prepared a series of bi-, tri- and tetra-dentate redox-active ferrocenylpyrazole ligands [11]; we prepared some ferrocene-containing enamine ligands and their transition metal complexes [12, 13]. We thought that it would be interesting to study metal complexes of bis-β-diketones with ferreocene. In this tetradentate ligand the ferrocenyl group plays the role of bridge between two potential coordination sites, which would incorporate ferrocene redox-active centers into variable

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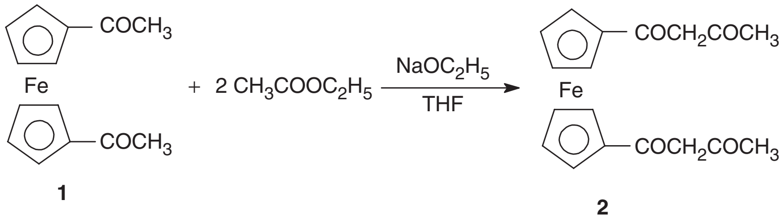

Scheme 1. Synthesis of 1,1′-bisacetylacetoferrocene.

multimetallic systems. Here we report our syntheses and crystal structures of transition metal complexes of 1,1′-bisacetylacetoferrocene.

2. Results and discussion

2.1. *Synthesis of 1,1′-bisacetylacetoferrocene*

Ferrocene-containing β-diketones are usually synthesized by Claisen condensation of acetylferrocene with appropriate ester compounds. The strong electron-donating properties of the ferrocenyl group lower the acidity of the methyl hydrogen atoms of acetylferrocene which in turn necessitates the use of strong bases to ensure reasonable yields. Thus sodium methoxide [4], potassium amide [5] or lithium diisopropylamide [6] were utilized as the active base in the reaction to give products in acceptable yields. For preparing ferrocene-containing bis-β-diketones, 1,1′-bisacetoferrocene was used, which was prepared by Friedel-Crafts reaction of ferrocene with acyl chloride catalyzed by aluminum trichloride. 1,1′-Bisacetylacetoferrocene has been prepared according to Claisen condensation routes [9, 10]. In our experiment sodium ethoxide in tetrahydrofuran was used as the basic system with some modifications to the published method. Sodium and ethanol react in fresh sodium-dried deoxygenated THF to form the sodium ethoxide solution. Then ethyl acetate was injected directly into the THF solution. After stirring for 10 min 1,1′-diacetylferrocene was added to the reaction system and the solution was refluxed for an additional 2 h. By using this procedure 1,1′-bisacetylacetoferrocene (**2**) was prepared in high yields (80%). In the ^{1}H NMR spectrum it displays enolic hydrogen signal at 15.86 ppm and ene hydrogen signal at 5.63 ppm, showing that the compounds exists in enolic form. In IR spectra it shows one stronger peak at 1622 cm^{-1}, indicating the carbonyl group and enol form intramolecular H-bonds. This is agreement with enolisation of the ferrocene-containing mono-β-diketones [14].

2.2. *Synthesis of transition metal complexes*

Transition metal complexes were prepared by stirring a mixture of methanolic solution of metal acetates $M(OAc)_2$ ($M = Mn^{2+}$, Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}) with a dichloromethane solution of ligand **2** for 5–6 h; the resulting precipitates were collected by filtration, washed with methanol and dried under vacuum. All complexes are deep red solids. Ligand **2** and metal complexes **3a–e** display very similar IR spectra with a sharp peak characteristic of the C=O bond at about 1620 cm^{-1}. UV spectra have more significant differences. Ligand **2** shows three peaks at 270, 307, 477 nm, which are due to charge transfer between cyclopentadienyl-iron atom and the carbonyl group, very similar to the UV spectra of monoacetylacetoferrocene (225, 305, 468 nm) [15]. Complexes **3a**–**e** also show two or three peaks with the band of carbonyl group shifting to lower field or becoming too weak to be seen coordinating to metal ions. This phenomena can also be found in the transition metal complexes of monoacetylacetoferrocene [15].

2.3. *X-ray diffraction analysis for 3a and 3b*

Crystals of **3a** and **3b** suitable for X-ray diffraction were grown from methanol solution. The crystal and structure refinement data are gathered in table 1. The molecular structures of **3a** and **3b** were shown in figures 2 and 3. Table 2 shows some selected geometric parameters. **3a** and **3b** were found to show very similar centrosymmetric cyclic dimers constituted by linkage of two Co^{2+} or Mn^{2+} ions and two 1,1′-diacetoacetylferrocene units. The so-formed macrocyclic framework was divided into two small cyclic units by two methanol bridges. Bimetallic complexes were formed instead of monometallic complexes formed by one 1,1′-diacetoacetylferrocene, indicating even if the two acetoacetyl groups at 1- and 1′-position of one ferrocene are *cis*, they still cannot coordinate to one metal. Recently it was reported that ferrocene-functionalized tetraazamacrocyclic ligands form monometallic complexes in which one more carbon chain existed in the side chain [16]. The octahedral coordination geometry around each metal is completed by four oxygen atoms from the two acetoactyl groups and two oxygen atoms of methanol. Because the crystal structures of

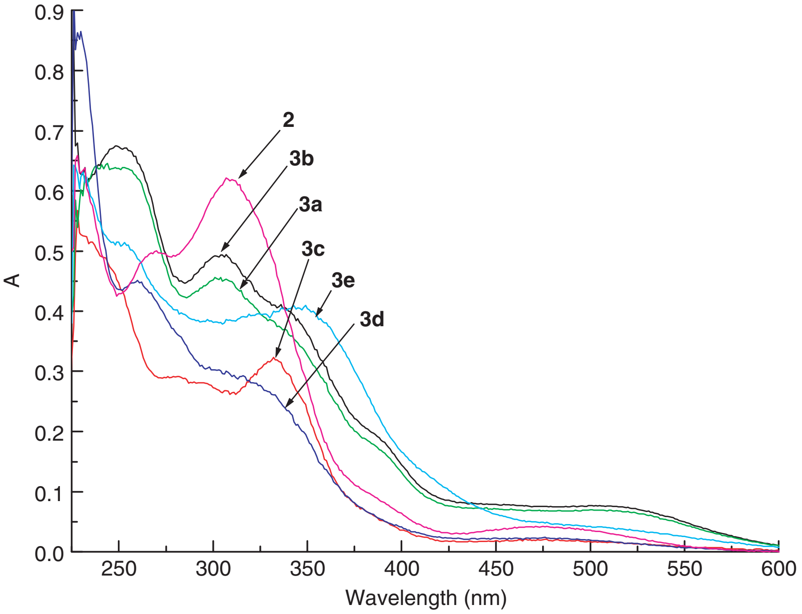

Figure 1. UV spectra of ligand **2** and complexes **3a**–**e**.

Table 1. Crystal data and structure refinement details for **3a** and **3b**.

	3a	**3b**
Chemical formula	$C_{38}H_{40}Co_2Fe_2O_{10}$	$C_{38}H_{40}Fe_2Mn_2O_{10}$
Formula weight	886.26	878.28
Crystal symmetry	Orthorhombic	Orthorhombic
Space group	*Aba*2	*Aba*2
Unit cell dimensions (Å, °)		
a	14.6280(2)	14.6374(2)
b	19.3511(3)	19.3544(3)
c	13.0484(3)	13.0555(3)
α	90.00	90.00
β	90.00	90.00
γ	90.00	90.00
Volume (Å^3)	3693.58(11)	3698.60(11)
Cell units Z	4	4
Crystal density (g cm^{-3})	1.594	1.577
Absorption coefficient (mm^{-1})	1.710	1.493
F (000)	1816	1800
Measurement temperature	296(2)	296(2)
Radiation_wavelength	0.71073	0.71073
Diffrn radiation type	Mo-Kα	Mo-Kα
θ range for data collection (°)	2.1–27.51	2.1–27.53
Limiting indices	$-19 \le h \le 18$; $-25 \le k \le 25$; $-16 \le h \le 16$	$-16 \le h \le 19$; $-22 \le k \le 25$; $-14 \le h \le 16$
Reflections collected/unique	4245/3385 [$R_{\text{int}} = 0.01$]	4010/2870 [$R_{\text{int}} = 0.02$]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4245/1/229	4010/1/229
Goodness-of-fit on F^2	1.051	1.029
Final R indices [$I > 2\sigma(I)$]	$R = 0.0610$, $wR = 0.1439$	$R = 0.0685$ $wR = 0.1325$
R indices (all data)	$R = 0.0488$, $wR = 0.1344$	$R = 0.0476$ $wR = 0.1242$
Largest differences peak and hole (e Å^{-3})	0.584 and −0.826	0.645 and −0.582

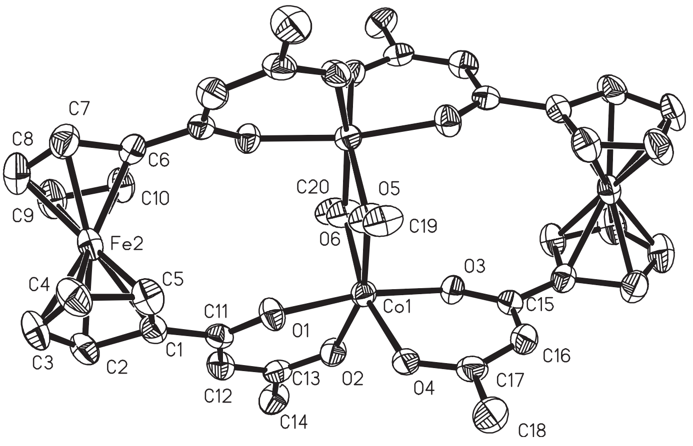

Figure 2. Crystal structure of complex **3a**. Hydrogen atoms are omitted for clarity.

3a and **3b** are nearly the same we would take **3a** as the example to discuss their structural details and similar observations can be realized on **3b**. In **3a** two Co^{2+} ions are bridged by two methanol molecules with an angle of O6–M1–O5 about 75.57(13)°. As typical for metal β-diketone complexes the six-membered ring ($C_3O_2M_1$) is planar.

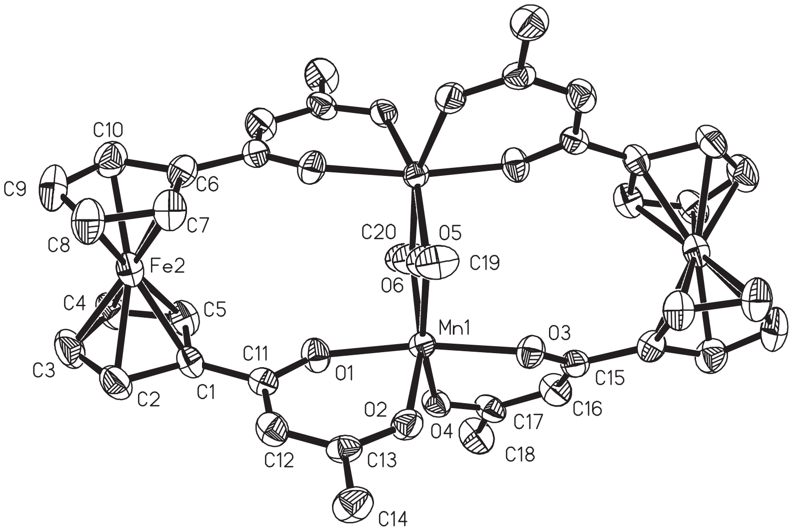

Figure 3. Crystal structure of complex **3b**. Hydrogen atoms are omitted for clarity.

Table 2. Selected geometric parameters (Å, °) for **3a** and **3b**.

	3a	**3b**
C1–C11	1.487(7)	1.487(7)
C11–C12	1.409(7)	1.396(8)
C12–C13	1.400(7)	1.378(7)
C13–C14	1.493(7)	1.508(7)
C11–O1	1.255(5)	1.265(6)
C13–O2	1.266(6)	1.281(6)
M1–O1	2.004(3)	2.003(4)
M1–O2	2.019(3)	2.009(4)
M1–O3	1.999(3)	2.002(3)
M1–O4	2.000(3)	1.996(3)
M1–O5	1.976(3)	1.990(3)
M1–O6	1.989(3)	1.975(3)
M1–M2		3.1327(11)
O6–M1–O5	75.57(13)	75.62(13)
O6–M1–O4	162.90(13)	91.65(16)
O5–M1–O4	91.66(15)	162.74(13)
O6–M1–O1	101.80(11)	84.53(10)
O5–M1–O1	84.58(10)	101.79(11)
O4–M1–O1	88.01(14)	88.28(14)
O3–M1–O1	170.83(14)	170.93(15)
O5–M1–O2	162.20(12)	93.12(16)
O4–M1–O2	101.76(14)	101.89(15)
O1–M1–O2	84.27(14)	84.21(15)
O1–C11–C12	123.1(4)	123.5(4)
O1–C11–C1	121.6(4)	113.9(4)
C13–C12–C11	122.4(4)	122.6(5)
O2–C13–C12	125.2(4)	125.4(5)
O2–C13–C14	114.8(5)	115.1(5)

The bond distances of C11–C12, C12–C13 are nearly the same at about 1.400 Å which indicate the extensive conjugation of enolate. The four Co–O distances of acetoacetyl groups are in the range of 1.999(3) to 2.019(3) Å, which are longer than the two Co–O distances of methanol oxygen within 1.976(3)–1.989(32) Å. It is very interesting that the two Cp rings in each ferrocene are nearly eclipsed and the two acetoacetyl residues are also in a cisoid conformation with the oxygen atoms pointing in opposite directions. The two acetoacetyl residues are nearly coplanar with the respective Cp ring. Fe–Cp distances rage from 2.032(4) to 2.057(4), intracyclopentadienyl C–C bond lengths lie in the range 1.413(5) to 1.444(5) and average C–C–C angles are very similar to those reported in the literature. There are very few crystal structure examples of metal complexes of ferrocene-containing bis-β-ketones, The crystal structure of mono-acetylacetoferrocene [17] and its rhodium complex [18] have been determined. The crystal structure of 1-acetoacetylferrocene showed that it existed in enol form with six atoms (C_3HO_2) of the side chain (CH_3COCH_2CO) in one plane, to forming a six-member ring and two oxygen atoms on the same side of the chains. Comparing the six-member coordinated ring (C_3O_2M) of rhodium complex of mono-acetylacetoferrocene with that of **3a** we find that the two C–O bond distances and two C–C bond distances are nearly the same and in the range observed in such enols for the C–O and C–C distances.

2.4. *Electrochemistry*

The voltammetric behavior of compounds **2**, **3a**–**e** on glassy carbon working electrodes was investigated in CH_2Cl_2, incorporating a saturated calomel reference electrode (SCE), and a platinum-wire auxiliary electrode. The electrochemical parameters for **2** and **3a**–**e** obtained from the CV are summarized in table 3 and figure. 4. The cyclic voltammetric behavior of all compounds showed one pair of well-defined and stable redox waves of the Fc/Fc$^+$ in the potential range of 0.0–1.1 V at the GC electrode and complexes **3a**–**c** show another pair of redox waves, which is attributed to the different redox state of metal ions. There is only one pair of redox waves of the Fc/Fc$^+$ in the complexes **3a**–**e** showing that the ferrocene moieties are equivalent, which can be seen from the symmetrical molecule structure of **3a** and **3b**. Comparing with the formal potentials ($E_{1/2}$) of ferrocene ($E_{1/2} = 0.437$) and 4-ferrocenylaniline ($E_{1/2} = 0.370$) [19], ligand **2** and complexes **3a**–**e** show increase of formal potential, suggesting that the electron withdrawing carbonyl group in **2** and **3a**–**e** significantly influence the redox potential of the iron center. That **2** has higher formal potential ($E_{1/2}^{1} = 0.874$) than that of the complexes, shows that the strong electron-withdrawing effect of carbonyl group,

Table 3. Electrochemical data of the complexes **3a**–**e**.

	E_{pa}^{1}	E_{pc}^{1}	$\Delta E_{\mathrm{p}}^{1}$	$E_{1/2}^{1}$	E_{pa}^{2}	E_{pc}^{2}	$\Delta E_{\mathrm{p}}^{2}$	$E_{1/2}^{2}$
2	0.907	0.846	0.061	0.874				
3a	0.928	0.813	0.115	0.871	0.650	0.071	0.579	0.361
3b	0.944	0.822	0.122	0.883	0.2	0.285	0.003	0.284
3c	0.903	0.825	0.078	0.864	0.704	0.704	0.060	0.734
3d	0.916	0.820	0.096	0.868				
3e	0.923	0.802	0.121	0.863				

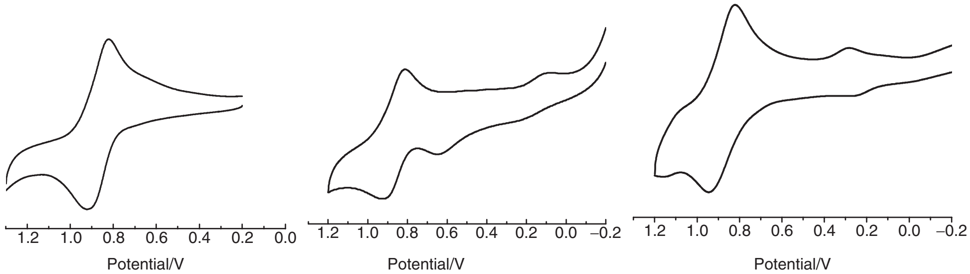

Figure 4. Cyclic voltammograms of **2** and **3a**, **3b**. Scan rate 50 mV S^{-1}.

weakens when coordinated with a metal ion. At the same time the formal potential of all five transition complexes **3a–e** are very close, indicating these five metallic ions have a similar electronic effect on the iron center and that all ferrocene subunits are in nearly equivalent environments. These electrochemical studies reveal that the redox potential of the iron center of ferrocene was influenced by the groups on the ferrocene units. The second pair of redox peaks in CVs of **3a–c** is due to redox properties of metal ions in different valence M^{n+}/M^{n+1}($M = Mn$, Co, Cu).

3. Conclusions

The ferrocene-containing bis-β-diketone tetradentate ligand 1,1′-bisacetylacetoferrocene and its five dinuclear transition metal complexes have been synthesized. Crystal structural analysis of complexes **3a** and **3b** indicate centrosymmetric macrocyclic dimeric frameworks constituted by a linkage of two Co^{2+} or Mn^{2+} ions and two 1,1′-diacetoacetylferrocene units with additional two methanol bridges. The cyclic voltammetric behavior of all compounds show one pair of well-defined and stable redox waves of the Fc/Fc^{+} suggesting that the electron withdrawing carbonyl group in **2** and **3a–e** significantly influence the redox potential of the iron center.

4. Experimental

All chemicals were of reagent grade obtained from commercial sources and used without further purification. The purity of all compounds was checked by TLC. The IR spectra of the ligand and complexes (4000–200cm^{-1}) in KBr discs were recorded on a Bruker Tensor 27 grating spectrophotometer. The ^{1}H NMR spectra were recorded on a Bruker AV-600 using $CDCl_3$ as solvent. The electrochemistry of complexes in CH_2Cl_2 was obtained using a CHI 660A electrochemical workstation (Shanghai). The UV-Vis spectra were recorded on a UV-Visible spectrophotometer (SHIMADZU).

4.1. *Synthesis of 1,1′-diacetylferrocene*

Under a nitrogen atmosphere to a 100 mL of flask, 40 mL of freshly distilled tetrahydrofuran, sodium sand (20.0 mmol, 0.460 g) and 5.0 mL of absolute ethanol was added. The mixture was stirred with heating till all sodium disappeared and then ethyl acetate (20.0 mmol, 1.96 g) was added. After 10 min the solid 1,1′-diacetylferrocene (10.0 mmol, 2.70 g) was added and the reaction mixture was refluxed for 2 h. The flask was cooled to room temperature and the yellow precipitate was filtered out and washed with absolute ethyl ether. The yellow solid was poured into 70 mL of water and acidified with acetic acid to yield the ligand **2**, as a deep red solid, 3.10 g (80%), m.p. 180°C; IR$\nu_{\max}$/cm^{-1}. 3450(w), 3121(w), 1736(w), 1622(vs), 1432(s), 1380(s), 1286(s), 1227(m), 1116(m), 1026(w), 941(w), 829(m), 787(m), 543(m). UV: 270.00(1.000×10^4), 307.00(1.242×10^4), 477.00(0.084×10^4) nm. ^{1}HNMR ($CDCl_3$) δ 2.09 (s, 6H, $2CH_3$); 4.49, 4.77 (s, s, 8H, $2C_5H_4$); 5.63 (s, 2H, 2CH); 15.86 (s, 2H, 2OH). Anal. Calcd for $C_{18}H_{18}O_4Fe$: C, 61.04; H, 5.12; Found: C, 61.23; H, 5.02.

4.2. *Synthesis of transition metal complexes*

Transition metal complexes **3a–e** were synthesized in similar fashion. A methanolic solution of metal acetate (0.05 mmol) was added with stirring to a dichloromethane solution of **2** (0.05 mmol, 0.178 g). The mixture was stirred for 5 to 6 h and the formed solid was filtered off, dried and washed with methanol several times, then stored in a vacuum dry box for analysis. The solution was filtered and allowed to evaporate slowly in air. Deep red crystals suitable for single crystal X-ray diffraction were isolated directly from solution after a few days.

3a, $Co_2L_2 \cdot 2CH_3OH$, deep red solid, yield 64%, IR ν: 3444(m), 1534(s), 1467(s), 1412(s), 1362(s), 1302(s), 1204(m), 1140(s), 1010(s), 961(m), 842(s), 778(m) cm^{-1}. UV: 244.00(1.292×10^4), 304.00(0.912×10^4), 500.00(0.140×10^4) nm. Anal. Calcd for $C_{38}H_{40}O_{10}Fe_2Co_2$: C, 51.50; H, 4.55; Found: C, 51.45; H, 5.02.

3b, $Mn_2L_2 \cdot 2CH_3OH$, deep red solid, yield 60%, IR ν: 3441(m), 1715(w), 1511(s), 1509(vs), 1456(s), 1732(s), 1286(s), 1217(m), 1134(m), 953(m), 801(s) cm^{-1}. UV: 249.00(1.349×10^4), 307.00(0.987×10^4), 501.00(0.154×10^4) nm. Anal. Calcd for $C_{38}H_{40}O_{10}Fe_2Mn_2$: C, 51.97; H, 4.59; Found: C, 51.54; H, 4.13.

3c, $Cu_2L_2 \cdot 2CH_3OH$, red brown solid, yield 70%. IR $\nu_{\max}$/cm^{-1}: 3424(m), 1552(s), 1513(vs), 1456(m), 1401(s), 1373(s), 1294(m), 1218(w), 1137(w), 1007(m), 812(m), 776(m), 656(w). UV: 332.00(0.647×10^4), 476.00($\times 10^4$) nm. Anal. Calcd for $C_{38}H_{40}O_{10}Fe_2Cu_2$: C, 50.97; H, 4.50; Found: C, 51.04; H, 5.02.

3d, $Ni_2L_2 \cdot 2CH_3OH$, red brown solid, yield 46%. IR $\nu_{\max}$/cm^{-1}: 3425(m), 2926(w) 1558(s), 1517(vs), 1456(m), 1387(s), 1285(s), 1218(w), 1137(w), 1113(m), 804(m), 596(w). UV: 260.00(0.902×10^4), 332.00(0.522×10^4), 476.00(0.048×10^4) nm. Anal. Calcd for $C_{38}H_{40}O_{10}Fe_2Ni_2$: C, 51.53; H, 4.55; Found: C, 51.04; H, 5.12.

3e, $ZnL_2 \cdot 2CH_3OH$, red brown solid, yield 56%. IR $\nu_{\max}$/cm^{-1}: 3499(m), 1591(m), 1526(s), 1488(s), 1455(m), 1308(m), 1204(m), 1083(w), 747(w), 703(m). UV: 257.00(1.004×10^4), 350.00(0.918×10^4) nm. Anal. Calcd for $C_{38}H_{40}O_{10}Fe_2Zn_2$: C, 50.78; H, 4.48; Found: C, 51.07; H, 4.77.

4.3. *Electrochemistry*

The voltammetric behaviors of compounds **2**, and **3a–e** of 10^{-3} M solutions in CH_2Cl_2 with 0.1 M Bu_4NClO_4 were recorded with a CHI 660A apparatus in a three electrode system, where glassy carbon was the working electrode, the reference was a saturated calomel reference electrode (SCE) and a platinum-wire electrode was auxiliary.

4.4. *X-ray structure determination*

The procedure of crystal structure determination for both **3a** and **3b** was the same. X-ray data were collected at 293(2) K on a Bruker Smart Apex 2 CCD diffractometer using Mo-Kα X-ray (0.71069 A°) source and a graphite monochromator. The unit cell dimensions were obtained from least-squares fit to setting angles of 25 reflections. Psi scan absorption corrections were applied. The structures were solved by direct methods using CRYSTAL STRUCTURE and refined by the full-matrix least squares method using SHELXL97. In the final step of refinement procedure, all non-hydrogen atoms were refined with anisotropic displacement parameters. Two hydrogen atoms of the amide group in **1** were found on the difference Fourier map. The other hydrogen atoms were introduced in calculated positions with idealized geometry and refined using a rigid body model. A summary of relevant crystallographic data is given in table 1.

Supplementary material

Single crystal X-ray diffraction data are deposited with CCDC (Deposition numbers 296441 for **3a** and 296442 for **3b**).

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