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Construction of Zn(II)-ferrocenyl carboxylate coordination complexes via changing adjuvant ligands

Jinpeng Li [a c] , Lu Liu [a] , Tingting Hou [a] , Huan Sun [a] , Yanyan Zhu [a] , Shaomin Wang [a] , Jinhong Wu [a] , Hong Xu [a] , Yuexin Guo [b] , Baoxian Ye [a] , Hongwei Hou [a] , Yaoting Fan [a] & Junbiao Chang [a c]

[a] Department of Chemistry , Zhengzhou University , Henan 450052 , P.R. China

[b] Department of Pharmacy , North China Coal Medicine University , Tangshan 063000 , P.R. China

[c] School of Pharmaceutical Sciences, Zhengzhou University , Henan 450052 , P.R. China

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Construction of Zn(II)-ferrocenyl carboxylate coordination complexes *via* changing adjuvant ligands

JINPENG LI†§, LU LIU†, TINGTING HOU†, HUAN SUN†, YANYAN ZHU†,
SHAOMIN WANG†, JINHONG WU†, HONG XU†, YUEXIN GUO‡,
BAOXIAN YE†, HONGWEI HOU*†, YAOTING FAN†
and JUNBIAO CHANG*†§

†Department of Chemistry, Zhengzhou University, Henan 450052, P.R. China
‡Department of Pharmacy, North China Coal Medicine University,
Tangshan 063000, P.R. China
§School of Pharmaceutical Sciences, Zhengzhou University, Henan 450052, P.R. China

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Five Zn(II)-ferrocenyl carboxylate complexes, $\{[Zn(OOCClH_3C_6Fc)(\eta^2OOCClH_3C_6Fc)(dpa)]\cdot(H_2O)\}$ (**1**), $[Zn(\eta^2\text{-}OOCClH_3C_6Fc)_2(2,2'\text{-dip})]\cdot(H_2O)_{0.25}\}$ (**2**), $\{[Zn(\eta\text{-}OOCClH_3C_6Fc)_2(bix)]_2\cdot(THF)\}$ (**3**), $[Zn(\eta\text{-}OOCClH_3C_6Fc)_2\cdot(Hfcz)]_n$ (**4**) and $\{[Zn(\eta\text{-}OOCClH_3C_6Fc)_2(H_2L_1)]\cdot(DMF)_2\}_n$ (**5**) [dpa = 2,2′-dipyridylamine, 2,2′-dip = 2,2′-bipyridine, bix = 1,4-bis(imidazol-1-ylmethyl)benzene, Hfcz = α-(2,4-difluorophenyl)-α-(1H-1,2,4-triazol-l-ylmethyl)-1H-1,2,4-triazole-l-ethanol, H_2L_1 = *N*,*N*′-bis(pyridin-4-yl)pyridine-2,6-dicarboxamide, Fc = ferrocene, $FcC_6H_3ClCOONa$ = sodium 2-chloro-4-ferrocenylbenzoic], have been synthesized and characterized. Single-crystal X-ray analysis reveals that **1** and **2** are mononuclear structures, **3** is a dimer, and **4** and **5** are 1-D structures. The five complexes exhibit some differences in their conformations, which can be attributed to the influence of adjuvant ligands. Notably, various π–π interactions as well as CH/π interactions are discovered in **1**–**5**, and they have significant contributions to self-assembly. The electrochemical properties of **1**–**5** indicate that half-wave potentials shift to positive potential compared with that of 2-chloro-4-ferrocenylbenzoic acid.

Keywords: Ferrocenyl carboxylate complexes; Nitrogen heterocyclic; Crystal structure; Electrochemical properties

1. Introduction

Design of coordination complexes has been a productive research area, owing to interesting molecular topologies and potential applications in multidisciplinary areas such as gas adsorption, separation, luminescent sensors, molecule magnets, and catalysts [1–6]. A variety of metal coordination complexes with interesting properties and topologies have been synthesized. However, it is still difficult to synthesize a desired metal–organic framework in a truly deliberate manner [7], owing to the influence of

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*Corresponding authors. Email: houhongw@zzu.edu.cn; changjunbiao@zzu.edu.cn

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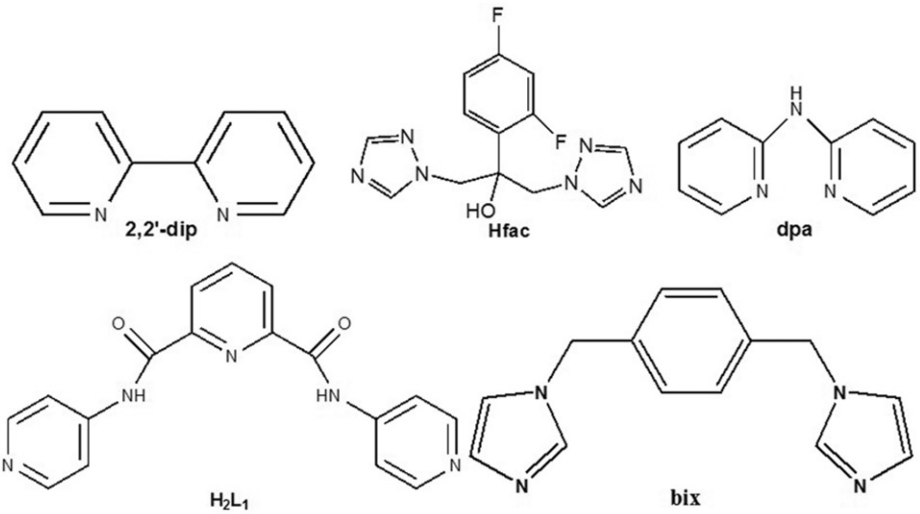
factors such as the structural characteristics of the ligand, metal/ligand ratio, and solvent system [8]. Ligands can adjust the coordinating modes, flexibility of the molecular backbone, configurational preference, type, and topology of the products by coordinating directly to the metal centers. Hence, the selection of ligand is crucial to construction of the resulting complexes [9]. Organic ligands with aromatic systems attract our ongoing interest because they may form various π–π and CH/π stacking interactions. These interactions have influence on controlling the conformation of molecules [10], crystal packing [11], molecular assembly into an organized supramolecular network [12–14], and the structure of proteins and DNA [15]. Ferrocenyl carboxylates with aromatic rings have strong coordinating capability, various coordination modes, and good electrochemical properties [16, 17], and are good choices to synthesize complexes. Recent investigations have demonstrated that use of mixed organic ligands, especially mixed carboxylate and N-containing ligands, is an effective strategy for construction of coordination complexes [18].

A series of nitrogen-heterocyclic ligands based on various aromatic systems (scheme 1) and 2-chloro-4-ferrocenylbenzoic acid were chosen to react with Zn(II) salts. Herein, we report the preparations and crystal structures of five new Zn(II) coordination complexes self-assembled by π–π stacking interactions and weak hydrogen bonds in combination with metal–ligand bonds. Electrochemical properties have also been investigated.

2. Experimental

2.1. *Materials and physical techniques*

2-Chloro-4-ferrocenylbenzoic acid and corresponding sodium salts were prepared by the method reported previously [19, 20]. 1,4-Bis(imidazol-1-ylmethyl)benzene (bix) was



Scheme 1. Basic N-containing organic subsidiary ligands used in text.

prepared according to the literature [21–23] and *N*,*N*′-bis(pyridin-4-yl)pyridine-2,6-dicarboxamide (H_2L_1) was synthesized by improving a literature method [24, 25]. All other chemicals were obtained from commercial sources and used without purification. Carbon, hydrogen, and nitrogen analyses were carried out on a FLASH EA 1112 elemental analyzer. IR data were recorded on a BRUKER TEN-SOR 27 spectrophotometer with KBr pellets from 400 to 4000 cm^{-1}. Cyclic voltammetric experiments were performed by employing a CHI 660B electrochemical analyzer. A three-electrode system was used, consisting of a platinum working electrode, a platinum wire auxiliary electrode, and an Hg/Hg_2Cl_2 reference electrode. The measurements were carried out in DMF solutions with tetrabutyl ammonium perchlorate (n-Bu_4NClO_4) (0.1 mol dm^{-3}) as supporting electrolyte. To prevent fouling, the working electrode was polished. Pure N_2 gas was bubbled through the electrolytic solution to remove oxygen.

2.2. *Synthesis of* $\{[Zn(\eta\text{-}OOCClH_3C_6Fc)(\eta^2\text{-}OOCClH_3C_6Fc)(dpa)]\cdot(H_2O)\}$ *(1)*

Methanol solution (4 mL) of dpa (8.2 mg, 0.05 mmol) was added to a methanol solution (2 mL) of $Zn(OAc)_2 \cdot 2H_2O$ (11.3 mg, 0.05 mmol), and then methanol solution (4 mL) of $FcC_6H_4ClCOONa$ (36.7 mg, 0.10 mmol) was added to the above mixture. The resulting mixture was kept at room temperature in the dark. About one week later, red crystals suitable for X-ray diffraction were obtained from the resultant orange solution. Yield: 55%. Anal. Calcd for $C_{44}H_{33}C_{12}Fe_2N_3O_{4.5}Zn$: C, 57.90; H, 3.90; N, 4.43. Found: C, 57.88; H, 3.95; N, 4.33%. IR (cm^{-1}, KBr): 3426(m), 1601(s), 1483(s), 1383(s), 1164(w), 1022(w), 833(m), 774(m), 488(m).

2.3. *Synthesis of* $\{[Zn(\eta^2\text{-}OOCClH_3C_6Fc)_2(2,2'\text{-}dip)]\cdot(H_2O)_{0.25}\}$ *(2)*

The procedure was the same as that for **1** with 2,2′-dip (7.4 mg, 0.05 mmol) used instead of dpa. Two weeks later, good quality red crystals were obtained from the resultant orange solution at room temperature in the dark. Yield: 43%. Anal. Calcd for $C_{44}H_{32}O_{4.25}N_2Fe_2ZnCl_2$: C, 58.36; N, 3.09; H, 3.54. Found: C, 58.49; N, 3.21; H, 3.72%. IR (cm^{-1}, KBr): 3418(s), 1600(s), 1460(m), 1393(s), 1105(w), 1043(m), 1015(m), 829(m), 746(m), 486(m).

2.4. *Synthesis of* $\{[Zn(\eta\text{-}OOCClH_3C_6Fc)_2(bix)]_2\cdot(THF)\}$ *(3)*

$FcC_6H_3ClCOONa$ (36.7 mg, 0.10 mmol) in methanol (4 mL) was added dropwise to the methanol solution (5 mL) of $Zn(OAc)_2 \cdot 2H_2O$ (11.3 mg, 0.05 mmol), and then methanol solution (5 mL) of bix (12.0 mg, 0.05 mmol) was slowly diffused into the above mixture. A moment later, tetrahydrofuran (1 mL) was added dropwise to the aforementioned mixture. The resulting solution was filtered to remove a small quantity of precipitation. One week later, red crystals suitable for X-ray diffraction were obtained from the resultant orange solution. Yield 48%. Anal. Calcd for $C_{50}H_{42}C_{12}Fe_2N_4O_{4.5}Zn$: C, 58.89; H, 4.12; N, 5.49. Found: C, 58.47; H, 3.96; N, 5.38%. IR (cm^{-1}, KBr): 3449(m), 3133(m), 1606(s), 1525(m), 1363(s), 1111(m), 1027(m), 830(s), 842(w), 757(w), 487(m).

2.5. *Synthesis of [Zn(η-OOCClH$_3$C$_6$Fc)$_2$•(Hfcz)]$_n$ (4)*

The procedure was the same as that for **1** with Hfcz (16.0 mg, 0.05 mmol) used instead of bix. The orange filtrate was kept at room temperature in the dark to evaporate to form red block crystals of **4** after several days in 49% yield. Anal. Calcd for $C_{47}H_{36}Cl_2F_2Fe_2N_6O_5Zn$: C, 53.67; H, 3.43; N, 7.99. Found: C, 53.42; H, 3.72; N, 7.67%. IR (cm^{-1}, KBr): 3238(m), 3143(m),1625(s), 1597(s), 1529(m), 1503(m), 1449(w), 1381(s), 1355(s), 1280(m), 1208(w), 1104(w), 1133(m), 1045(w), 848(m), 789(m), 655(m), 491(m).

2.6. *Synthesis of {[Zn(η-OOCClH$_3$C$_6$Fc)$_2$(H$_2$L$_1$)]•(DMF)$_2$}$_n$ (5)*

DMF solution (4 mL) of H_2L_1 (32 mg, 0.1 mmol) was added to a methanol solution (3 mL) of $Zn(NO_3)_2 \cdot 6H_2O$ (29 mg, 0.1 mmol), and then methanol solution (3 mL) of $FcC_6H_4ClCOONa$ (72 mg, 0.2 mmol) was added to the above mixture. The resulting solution was filtered to remove a small quantity of precipitation. Two days later, red crystals suitable for X-ray diffraction were obtained from the resultant red solution. Yield: 75%. Anal. Calcd for $C_{57}H_{47}C_{12}Fe_2N_7O_8$ Zn: C, 56.72; H, 3.89; N, 8.13. Found: C, 57.23; H, 3.95; N, 7.99%. IR (cm^{-1}, KBr): 3426(m), 3256(s), 3088(m), 1702(s), 1658(s), 1600, 1583(s), 1126(m).

2.7. *Crystal structure determination*

A crystal suitable for X-ray determination was mounted on a glass fiber. The data of **1**–**5** were collected on a Rigaku Saturn 724 CCD diffractomer (Mo-Kα, $\lambda = 0.71073$ Å) at 20 ± 1°C. The structures were solved by direct methods and expanded with Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. All calculations were performed with the SHELXL-97 crystallographic software package [26]. Table 1 shows crystallographic crystal data and processing parameters for all complexes and table 2 lists their selected bond lengths and angles.

3. Results and discussion

3.1. *Crystal structures of {[Zn(OOCClH$_3$C$_6$Fc)(η^2-OOCClH$_3$C$_6$Fc)(dpa)•(H$_2$O)} (1) and {[Zn(η^2-OOCClH$_3$C$_6$Fc)$_2$(2,2′-dip)]•(H$_2$O)$_{0.25}$} (2)*

Treatment of $FcC_6H_3ClCOONa$ with $Zn(OAc)_2 \cdot 2H_2O$ in the presence of dpa yielded **1**. Crystallographic analysis reveals that **1** crystallizes in the triclinic space group $P\bar{1}$ and exhibits a mononuclear structure owing to the influence of chelating dpa. $FcC_6H_3ClCOO^-$ units display two kinds of coordination: bidentate-chelating (η^2-OOCClH$_3$C$_6$Fc) and monodentate coordinated (η-OOCClH$_3$C$_6$Fc). Each penta-coordinated Zn(II) ion is connected by three oxygen atoms (figure 1a), of which two are from one η^2-OOCClH$_3$C$_6$Fc, the other is from monodentate $FcC_6H_3ClCOO^-$, and two nitrogen atoms from one dpa. The Zn–O$_{(OOCClH3C6Fc)}$ bond lengths are 1.921(3) Å,

Table 1. Crystal data and structure refinement for **1–5**.

Complexes	**1**	**2**	**3**	**4**	**5**
Formula	$C_{44}H_{33}Cl_2Fe_2N_3O_6Zn$	$C_{44}H_{32}Cl_2Fe_2N_2O_{4.25}Zn$	$C_{50}H_{42}Cl_2Fe_2N_4O_{4.50}Zn$	$C_{114}H_{94}Cl_4Fe_4N_{14}O_{16}Zn_2$	$C_{188}H_{144}Cl_8F_8Fe_8N_{24}O_{20}Zn_4$
Formula weight	947.70	904.69	1018.85	2411.97	4203.15
Temperature (K)	293(2)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P2(1)/c$	$C2/c$
Unit cell dimensions (Å, °)					
a	10.803(2)	34.517(7)	12.886(3)	23.049(5)	30.505(6)
b	12.502(3)	8.6071(17)	13.028(3)	12.357(3)	17.630(4)
c	15.637(3)	13.485(3)	16.112(3)	23.143(5)	17.995(4)
α	102.36(3)	90	89.96(3)	90	90
β	103.11(3)	110.57(3)	79.18(3)	116.60(3)	107.11(3)
γ	96.42(3)	90	64.62(3)	90	90
Volume (Å^3), Z	1980.5(7), 2	3751.0(13), 4	2390.6(8), 2	5894(2), 2	9249(3), 2
Calculated density (g cm^{-3})	1.589	1.602	1.415	1.359	1.509
$F(000)$	964	1840	1044	2472	4272
θ range for data collection (°)	3.22–27.46	3.03–24.99	3.01–25.00	3.05–27.49	3.08–27.48
Reflections collected/unique	24,140/8996	18,070/3282	24,382/8410	69,278/13477	55,555/10,559
Data/restraints/parameters	8996/0/643	3282/0/255	8410/46/578	13,477/40/739	10,559/0/587
Goodness-of-fit on F^2	1.124	1.065	1.066	1.002	1.175
Final R_1[a], wR_2[b]	0.0539, 0.1194	0.0325, 0.0876	0.0750, 0.2077	0.0731, 0.1967	0.0707, 0.2115

[a] $R_1 = ||F_o| - |F_c|/|F_o|$; [b] $wR_2 = [w(|F_o^2| - |F_c^2|)^2/w|F_o^2|^2]^{1/2}$; $w = 1/[\sigma^2(F_o)^2 + 0.0297P^2 + 27.5680P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected bond lengths (Å) and angles (°) for **1–5**.

Complex **1**					
N(1)–Zn(1)	2.017(4)	O(1)–Zn(1)	2.264(7)	Zn(1)–O(3)	1.921(3)
Zn(1)–N(3)	2.029(4)	Zn(1)–O(2)	2.160(6)	O(3)–Zn(1)–N(1)	119.91(19)
O(3)–Zn(1)–N(3)	114.68(17)	N(1)–Zn(1)–N(3)	91.92(16)	O(3)–Zn(1)–O(2)	114.99(19)
Complex **2**					
Zn(1)–O(1)#1	2.067(2)	Zn(1)–O(1)	2.067(2)	Zn(1)–N(1)	2.093(2)
Zn(1)–N(1)#1	2.093(2)	Zn(1)–O(2)	2.302(2)	Zn(1)–O(2)#1	2.302(2)
O(1)#1–Zn(1)–O(1)	135.26(11)	O(1)#1–Zn(1)–N(1)	104.11(8)	O(1)–Zn(1)–N(1)	110.30(8)
O(1)#1–Zn(1)–N(1)#1	110.30(8)	O(1)–Zn(1)–N(1)#1	104.12(8)	N(1)–Zn(1)–N(1)#1	78.18(12)
Complex **3**					
Zn(1)–O(3)	1.959(4)	Zn(1)–O(1)	1.972(4)	Zn(1)–N(1)	2.005(4)
Zn(1)–N(3)	2.019(5)	O(3)–Zn(1)–O(1)	113.08(17)	O(3)–Zn(1)–N(1)	94.39(18)
O(1)–Zn(1)–N(1)	113.82(17)	O(3)–Zn(1)–N(3)	108.70(19)	O(1)–Zn(1)–N(3)	110.29(18)
Complex **4**					
Zn(1)–O(3)	1.927(4)	Zn(1)–O(2)	1.959(3)	Zn(1)–N(6)#1	2.034(4)
N(1)–Zn(1)	2.016(4)	O(3)–Zn(1)–O(2)	116.80(15)	O(3)–Zn(1)–N(1)	114.60(17)
O(2)–Zn(1)–N(1)	112.29(16)	O(3)–Zn(1)–N(6)#1	112.04(17)	O(2)–Zn(1)–N(6)#1	97.27(16)
Complex **5**					
Zn(1)–O(6)	1.923(3)	Zn(1)–O(3)	1.953(3)	Zn(1)–N(4)	2.024(4)
Zn(1)–N(5)	2.054(4)	O(6)–Zn(1)–O(3)	116.22(16)	O(6)–Zn(1)–N(4)	121.73(16)
O(3)–Zn(1)–N(4)	101.78(15)	O(6)–Zn(1)–N(5)	104.84(16)	O(3)–Zn(1)–N(5)	107.39(16)

Symmetry transformations used to generate equivalent atoms: for **2**: #1 $-x$, y, $-z+1/2$ and for **4**: #1 x, $-y+1$, $z-1/2$.

shorter than those of $\mathrm{Zn{-}O}_{(\eta 2\text{-}\mathrm{OOCClH3C6Fc})}$ [2.264(7) Å and 2.160(6) Å]. The Zn–N (dpa) bond lengths are 2.029(4) Å and 2.017(4) Å, respectively. The π–π interactions play a crucial role in molecular self-assembly. Analysis of the crystal packing of **1** revealed that an infinite 2-D supramolecular network (figure 1b) was formed by head-to-tail π–π stacking interactions between two adjacent dpa rings, with interplanar separation of 3.33 Å (center-to-center separation: 3.65 Å) [27]. Between adjacent ferrocene rings, an interesting feature is that both types of aromatic π–π stacking interactions are observed. One type is the head-to-tail π–π stacking interactions from intermolecular ferrocene rings with interplanar separation of 3.51 Å (center-to-center separation: 3.66 Å). Another type of edge-to-face CH/π interaction between two adjacent ferrocene rings is 2.84 Å with dihedral angle of 75.3° (H/π-plane separation: 2.74 Å). There are similar edge-to-face CH/π interactions between intermolecular ferrocene rings and pyridine rings. The distance is 2.69 Å with dihedral angle of 78.4° (H/π-plane separation: 2.63 Å). Additionally, intermolecular O···H···O hydrogen bonds are observed in **1**. The O···O distances of the hydrogen bonds are 2.877 Å and the bond angles O···H···O are 161.41°. Stacking interactions and O···H···N [2.877(6) Å] hydrogen-bonding interactions (figure 1c) interconnect separate mononuclear structures to produce a 3-D supramolecular framework.

Similarly, when we utilize 2,2′-dip instead of dpa to react with $\mathrm{FcC_6H_3ClCOONa}$, **2** is obtained. X-ray diffraction analysis reveals that **2** crystallizes in the monoclinic space group $C2/c$. As depicted in figure 2(a), Zn(II) is six-coordinate in a distorted octahedral environment with four oxygen atoms from two η^2-$\mathrm{FcC_6H_3ClCOO^-}$ units and two nitrogen atoms from one 2,2′-dip. The bond angles around Zn(II) vary from 59.76(8)° to 157.79(8)°. The Zn–N lengths are 2.093(2) Å. The Zn–O lengths are 2.067(2)–2.302(2) Å. Both carboxylate groups of $\mathrm{FcC_6H_3ClCOO^-}$ anions and 2,2′-dip adopt

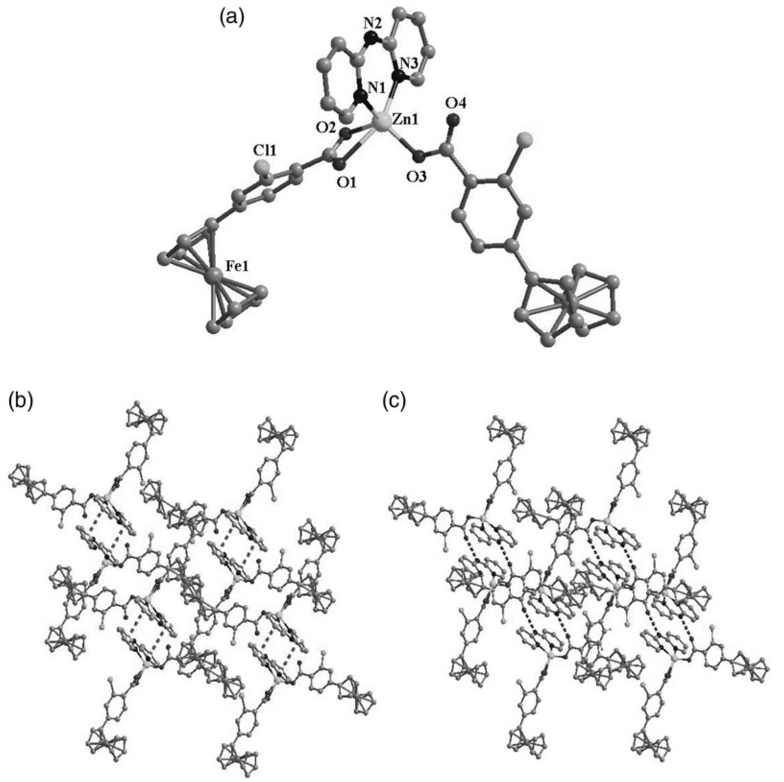


Figure 1. (a) Crystal structure of {[Zn(OOCClH$_3$C$_6$Fc)(η^2-OOCClH$_3$C$_6$Fc)(dpa)]·(H$_2$O)} (**1**). (b) View of two complexes showing π–π interactions between the dpa rings. (c) View of hydrogen bonds between two molecules with O···N distance of 2.878 Å (hydrogen atoms and solvent omitted for clarity).

bidentate chelating coordination, which results in forming mononuclear **2**. For **2**, no hydrogen bonds exist, but there are the same aromatic ring systems as in **1**. Between the same aromatic rings, similar π–π and CH/π stacking interactions are also formed. First, between pyridine rings of two adjacent 2,2′-dip, there are the π–π interactions with average interplanar distance of 3.49 Å [center-to-center separation: 3.86 Å (figure 2b–A)]. Between intermolecular benzene rings and ferrocene rings, π–π interactions with average interplanar distance of 3.13 Å [center-to-center separation: 3.85 Å (figure 2b–B)] is stronger than that of two adjacent pyridine rings. Second, between adjacent ferrocene rings, there are two kinds of edge-to-face CH/π interactions. One is 2.84 Å with dihedral angle of 101.9° (H/π-plane separation: 2.77 Å) and the other is 2.90 Å with dihedral angle of 118.1° (H/π-plane separation: 2.56 Å). The π–π interactions are important in **1** and **2**, contributing significantly to molecular self-assembly.

3.2. *Crystal structures of {[Zn(η-OOCClH$_3$C$_6$Fc)$_2$(bix)]$_2$•(THF)} (3)*

Complex **3** is a neutral binuclear molecule composed of two Zn(II) cations, two bix ligands, and four FcC$_6$H$_3$ClCOO$^-$ anions (figure 3a). The molecule crystallizes in the

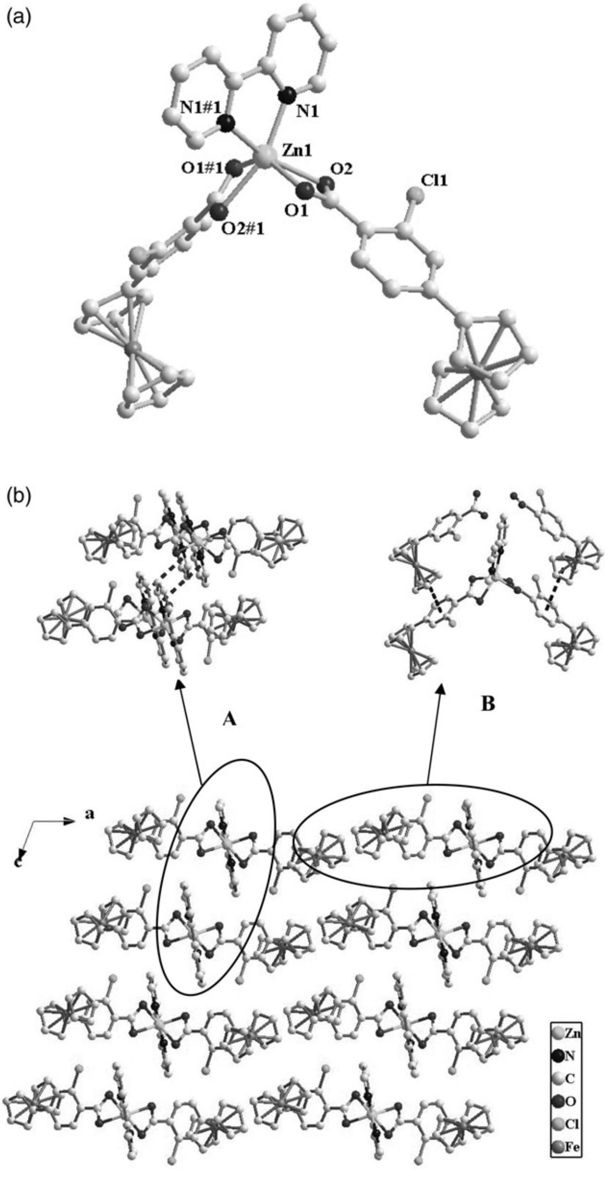


Figure 2. (a) Perspective view of [Zn(η^2-OOCClH$_3$C$_6$Fc)$_2$(2,2′-dip)]·(H$_2$O)$_{0.25}$} (**2**). (b) View of packing diagram of **2** showing extensive hydrogen-bonding and π–π interactions. Hydrogen atoms are omitted for clarity in (a) and (b).

triclinic space group $P\bar{1}$. Each Zn(II) is four-coordinate in a distorted tetrahedron with two oxygen atoms from two monodentate chelate FcC$_6$H$_3$ClCOO$^-$ groups and two nitrogen atoms from two bix. Owing to semirigid character, bix often adopts stable *cis*/*trans*-conformation. In **3**, two bix ligands have symmetric *cis*-conformation, bonding separate Zn(II) centers through nitrogen atoms, generating a binuclear structure with 26-member rings. The Zn1–N bond lengths are 2.005(4) and 2.019(5) Å, and Zn1–O

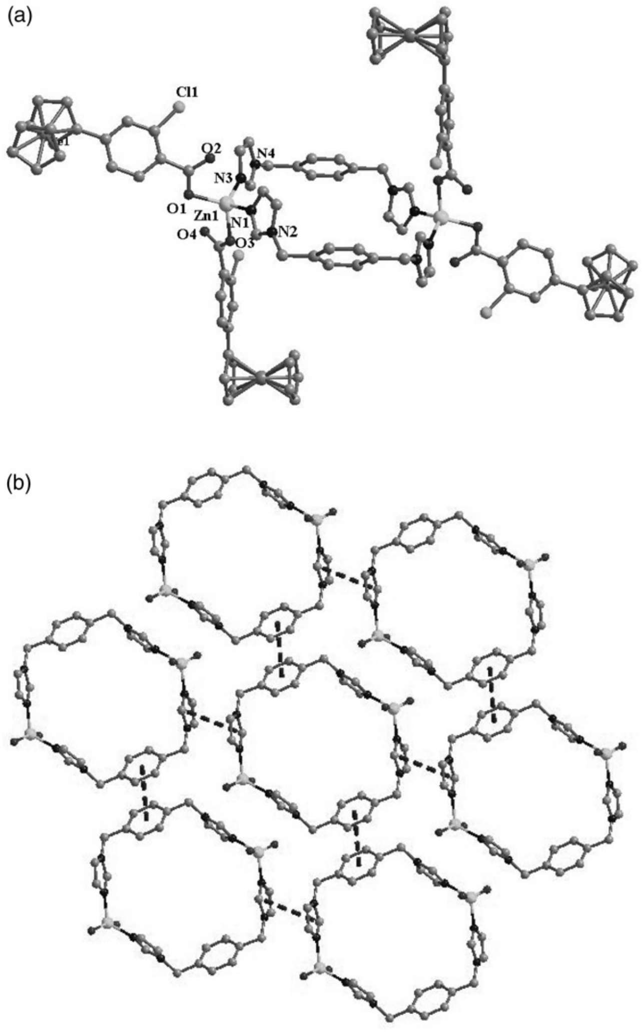


Figure 3. (a) Perspective view with partial atom-labeling of the binuclear structure of $\{[Zn(\eta\text{-}OOCClH_3C_6Fc)_2(bix)]_2{\cdot}(THF)\}$ (**3**). Hydrogen atoms and solvent are omitted for clarity. (b) View of the infinite 2-D supramolecular structure of **3**.

bond lengths are 1.959(4) and 1.972(4) Å. Zn–N distances are slightly shorter than those of reported Zn(II) coordination complexes, showing strong interactions between Zn and N. For example, $[Zn(4,4'\text{-bipy})(H_2O)_3(ClO_4)](ClO_4){\cdot}(4,4'\text{-bipy}){\cdot}1.5H_2O$ [Zn–N: 2.104(2)–2.117(2) Å] [28a], $[Zn(tp)(4,4'\text{-bipy})]$ [tp = terephthalate] [Zn–N: 2.154(2)–2.186(3) Å] [28b] and $\{[Zn(fca)_2(bpe)]\cdot(H_2O)_2\}_n$ [fca = $C_5H_5FeC_5H_4C(OH)CHCOCH_3$] [Zn–N: 2.196(8)–2.205(8) Å] [28c]. The bond angles around each Zn(II) range from 94.39(18)° to 115.62(19)°. Hence, average bond angle at Zn1 is 109.4°, slightly smaller than 109.5° for an ideal tetrahedron. The Zn···Zn distance in **3** is 10.585 Å. Between two adjacent $[Zn(OOCClH_3C_6Fc)_2(bix)]_2$ units, benzene rings are parallel with average interplanar distance of 3.82 Å [center-to-center separation: 4.08 Å], which is in the range of normal π–π interactions [27]. These weak π–π

interactions result in a 2-D infinite packing structure (figure 3b). Triazole rings are also parallel with average interplanar distance of 3.46 Å [center-to-center separation: 3.97 Å]. Similar to **1** and **2**, various CH/π interactions also exist in **3**. For instance, between intermolecular ferrocene rings, there are CH/π interactions at 2.93 Å (dihedral angle: 107.2°; H/π-plane separation: 2.74 Å). Between adjacent ferrocene and benzene rings of bix, the CH/π interaction is 2.80 Å (dihedral angle: 101.9°; H/π-plane separation: 2.68 Å). There are also such interactions at 2.95 Å (dihedral angle: 102.4°; H/π-plane separation: 2.87 Å) between solvent molecules and triazole rings. These weak interactions lead to a 3-D supramolecular structure.

3.3. *Crystal structures of* $[Zn(\eta\text{-}OOCClH_3C_6Fc)_2\cdot(Hfcz)]_n$ *(4) and* $\{[Zn(\eta\text{-}OOCClH_3C_6Fc)_2(H_2L_1)]\cdot(DMF)_2\}_n$ *(5)*

Complex **4** features a 1-D chain and crystallizes in the monoclinic space group *P*2(1)/*c*. Each four-coordinate Zn(II) ion has a distorted tetrahedral environment with two oxygen atoms from two monodentate chelate $FcC_6H_3ClCOO^-$ groups and two nitrogen atoms from two Hfcz (figure 4a). The Zn1–N bond lengths are 2.016(4) and 2.034(4) Å, and Zn1–O bond lengths are 1.927(4) and 1.959(3) Å. The bond angles around Zn(II) vary from 97.27(16)° to 116.80(15)°. Each Hfcz bridges two Zn(II) with its two *exo*-N-donors in a *trans*-conformation to give a 1-D zigzag chain as depicted in figure 4(a). Complex **5** has a similar crystal structure, but different space group *C*2/*c* than **2**; the local environment around zinc is shown in figure 5(a). Each Zn(II) is a distorted tetrahedral with two oxygen atoms from two $FcC_6H_3ClCOO^-$ groups in monodentate chelate mode and two nitrogen atoms from two H_2L_1. The Zn1–N bond lengths are 2.024(4) Å and 2.054(4) Å, and Zn1–O bond lengths are 1.923(3) Å and 1.953(3) Å. The bond angles around each Zn(II) are 101.78(15)–121.73(16)°. Each H_2L_1 is bidentate linking two Zn(II) to form a 1-D wave-shaped chain (figure 5b). Parallel chains are illustrated in figure 5(c).

For **4** and **5**, there are also various aromatic ring systems which form similar CH/π interactions. In **4**, because of Hfcz, there are intramolecular edge-to-face CH/π interactions 2.79 Å (dihedral angle: 119.8°; H/π-plane separation: 2.34 Å) between triazole rings and ferrocene rings. Meanwhile, between intermolecular ferrocene rings and phenyl rings of $FcC_6H_3ClCOO^-$ ligand, there are edge-to-face CH/π interactions 2.86 Å (dihedral angle: 107.6°; H/π-plane separation: 2.70 Å). Between two adjacent chains, such 1-D chains are further extended into a 3-D supramolecular framework along the *ab*-plane through O···H···O hydrogen bonds (figure 4b) with O···O distance of 2.737(9) Å (bond angles of 174.95°) and intermolecular CH/π interactions. In **5**, there is no direct hydrogen-bonding but CH/π interactions among benzene rings, ferrocene rings, and pyridine rings. Between ferrocene rings and pyridine rings of adjacent H_2L_1, edge-to-face CH/π interaction is 2.97 Å (dihedral angle: 68.6°; H/π-plane separation: 2.70 Å). Between pyridine rings of adjacent H_2L_1, edge-to-face CH/π interaction is 2.85 Å (dihedral angle 82.5°; H/π-plane separation: 2.81 Å). Between adjacent ferrocene rings, there are also edge-to-face CH/π interactions at 3.06 Å (dihedral angle: 79.7°; H/π-plane separation: 2.99 Å). Finally, between intermolecular ferrocene rings and phenyl rings of H_2L_1, the interplanar separation is 3.35 Å (center-to-center separation: 3.85 Å). These interactions play an important role in molecular self-assembly, which results in 3-D supramolecular frameworks.

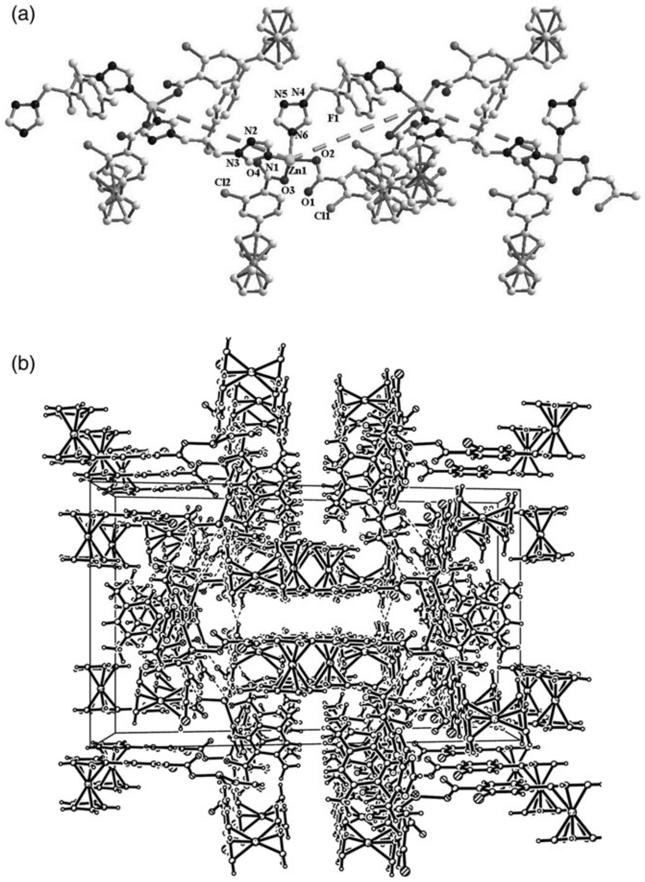


Figure 4. (a) View of 1-D zigzag chain of $[Zn(\eta\text{-}OOCClH_3C_6Fc)_2 \cdot (Hfcz)]_n$ (**4**). Hydrogen atoms and solvent are omitted for clarity. (b) View of the infinite 3-D supramolecular structure of **4** with O···H···O (2.737(9) Å) hydrogen bonds.

3.4. *Electrochemical properties*

The electrochemical behaviors of **1**–**5** have been studied by cyclic voltammetry and differential pulse voltammograms (DPVs) in DMF (*ca* $5.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$ total Fc concentrations) containing $0.1\,\mathrm{mol\,L^{-1}}$ n-Bu_4NClO_4 as the supporting electrolyte (as shown in figure 6). From the cyclic voltammograms (CVs) (figure 6a), **1**–**5** and sodium 2-chloro-4-ferrocenylbenzoate exhibit a quasi-reversible redox wave. Solution-state DPVs (figure 6b) show that **1**–**5** have a single peak, which can be assigned to electron-transfer of the ferrocenyl moiety. The half-wave potential ($E_{1/2}$) of the 2-chloro-4-ferrocenylbenzoic acid is 0.544 V. Compared with ferrocenyl carboxylates, $FcCH{=}CHCOOH$ (0.620 V in DMF solution) and $FcCOC_2H_4COOH$ (0.716 V in DMF solution), the half-wave potential of $FcC_6H_3ClCOOH$ (0.544 V) is shifted to lower potential. This behavior is from the presence of the phenyl ring between the electroactive ferrocene and carboxyl group. The electron-donating ability of the conjugated phenyl serves to partially counteract the electron-withdrawing inductive

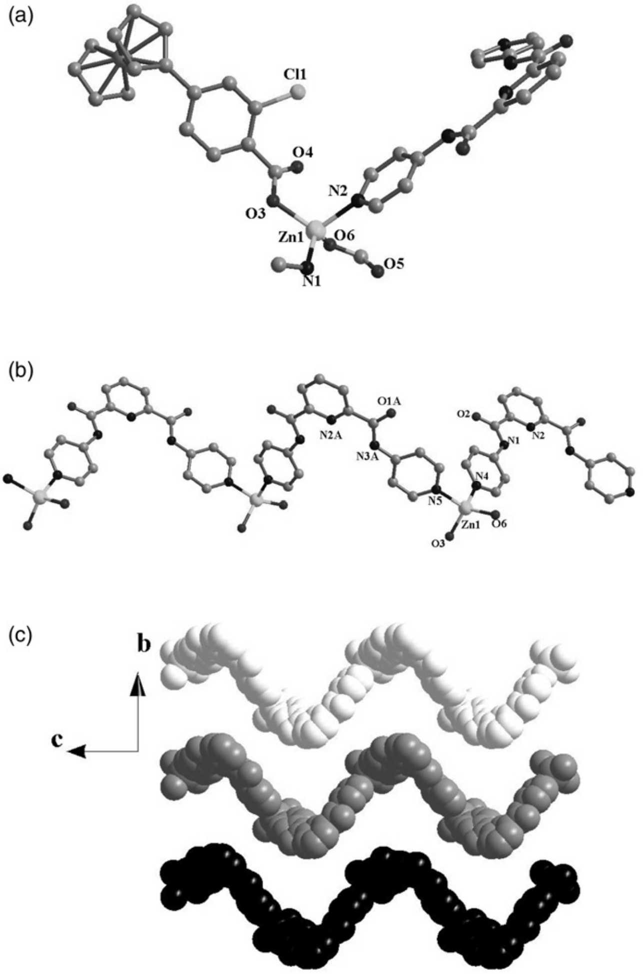


Figure 5. (a) Coordination geometry of the Zn(II) center in **5**. (b) 1-D wave-shaped chain of **5** (partial $FcC_6H_3ClCOO^-$, H_2L_1 units, hydrogen atoms and solvent are omitted for clarity). (c) The packing perspective view of **5** along the *a*-axis.

effect of the carboxyl and metal [29–31]. The solution-state DPVs (figure 6b) of **1**–**5** show a single peak with a half-wave potential ($E_{1/2}$ *vs.* SCE) at 0.552 V for **1**, 0.552 V for **2**, 0.568 V for **3**, 0.556 V for **4**, and 0.560 V for **5**, all shifted to higher potentials in contrast with that of free $FcC_6H_3ClCOOH$, consistent with previous results [32–38]. The central metal in these complexes have some influence on the half-wave potential of the ferrocenyl moieties, and the electron-withdrawing nature of the coordinated metal centers make the ferrocene harder to oxidize [39, 40]. Different electron-withdrawing nature of N-containing ligands also has slight influence on the half-wave potential of the ferrocenyl moieties, so the half-wave potentials of these Zn(II) complexes display some differences. Incorporation of carboxyl, metal, and N-containing ligands make FeII/FeIII oxidation potential of ferrocene-containing complexes have positive shifts.

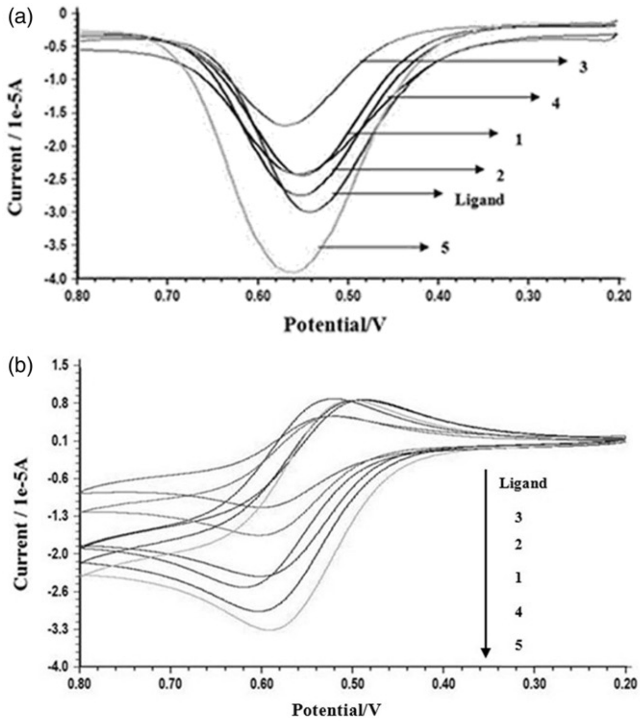


Figure 6. CVs (a) and DPVs (b) of **1–5** and $FcC_6H_3ClCOOH$ (ligand) in DMF-containing n-Bu_4NClO_4 ($0.1\,mol\,L^{-1}$).

4. Conclusion

A series of Zn(II)-containing coordination complexes based on 2-chloro-4-ferrocenylbenzoic acid were synthesized and structurally characterized. Complexes **1–5** are characterized by various aromatic ring systems that can easily form weak interactions, such as π–π interactions, CH/π interactions, and hydrogen bonds, expanding **1–5** to 3-D supramolecular networks. The results indicate that selection of mixed ligands with aromatic systems is an effective synthetic strategy to construct complexes.

Supplementary material

Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication with CCDC numbers 869067, 869068, 869069, 869070, and 869071 (**1**, **2**, **3**, **4**, and **5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (44) 1 223 336-033; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

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