PAPER

NJC
www.rsc.org/njc

Novel zinc(II) coordination polymers constructed from ferrocenyl carboxylate ligands†

Gang Li, Hongwei Hou,* Zifeng Li, Xiangru Meng and Yaoting Fan

Department of Chemistry, Zhengzhou University, 450052 Henan, P. R. China. E-mail: houhongw@zzu.edu.cn

Received (in Montpellier, France) 8th May 2004, Accepted 6th August 2004
First published as an Advance Article on the web 22nd November 2004

Two novel ferrocene-containing Zn(II) coordination polymers, $[Zn\{\mu_2\text{-}OOCCH{=}(CH_3)CFc\}_2]_n$ [**1**, Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$] and $\{[Zn_2\{\mu_2\text{-}OOCCH{=}(CH_3)CFc\}_4(bpa)]\cdot 2MeOH\}_n$ [**2**, bpa = 1,2-bis (4-pyridyl)ethane], have been prepared. The two polymers have been characterized by single-crystal X-ray crystallography. The Zn(II) ions in polymer **1** are bridged by μ_2-coordinated $FcC(CH_3){=}CHCOO^-$ anions, forming an infinite $[Zn(\mu_2\text{-}OOCH{=}(CH_3)CFc\}_2]_n$ chain. Polymer **2** is constructed from paddle-wheel shaped $[Zn_2\{\mu_2\text{-}OOCCH{=}(CH_3)CFc\}_4]$ building units. The dimeric tetrabridged cores are connected by organic bridging ligands, leading to a linear $[Zn_2\{\mu_2\text{-}OOCCH{=}(CH_3)CFc\}_4(bpa)]_n$ chain. To the best of our knowledge, **2** is the first example of a Zn(II) polymer built up by ferrocene-based paddle-wheel building units. The electrochemical properties of both polymers were also investigated.

Introduction

Recently, there has been an upsurge of research into coordination polymers[1–14] due to their potential applications in various areas, such as molecular recognition,[15] host–guest chemistry,[16] nonlinear optics,[17] molecular magnetic materials,[18] catalysis,[19] and electronic devices.[20] By utilizing various multifunctional ligands, changing counterions or the solvent used or synthetic methods, a remarkable variety of polymeric frameworks with intriguing topologies have been prepared.

In this context, Zn-containing coordination polymers have also attracted much attention due to their potential applications in the preparation of luminescent and nonlinear optical materials.[3,21] In 2003, Erxleben has given a detailed description of the structures and properties of Zn(II) coordination polymers,[3] which can generally by classified into six types according to the different ligands used: (1) rigid bi-connecting ligands, (2) rigid trigonal connectors, (3) carboxylates, pyridine carboxylates and pyrazine carboxylates, (4) secondary building blocks, (5) conformationally flexible ligands, and (6) phosphate ligands. Although numerous Zn(II) coordination polymers have been published, the reports of Zn(II) polymers that contain ferrocenyl group are very limited.[21] Recently, Mochida *et al.* have synthesized two Zn(II) coordination polymers containing pyridine-based ferrocene ligands.[21a,b] We have also reported a one-dimensional (1-D) polymer, $\{[Zn(fca)_2(bpe)]\cdot 2H_2O\}_n$ [fcaH = 1-ferrocenylbutane-1,3-dione, bpe = 1,2-bis(4-pyridyl)ethene], in which enolized ferrocenylacetone ligands chelate the Zn centers while bpe serves as a bridging ligand.[21c] Zn(II) polymers generated by ferrocenyl-substituted carboxylate ligands have also been reported.[21d–f] Although considerable efforts have been devoted to introduce the ferrocenyl group into coordination polymer systems because of the special chemical, stereochemical, and electrochemical properties of the ferrocene moiety,[22] structural characterizations of ferrocene-based polymers are generally difficult to carry out.[21b]

More recently, we have reported that the long $-C(CH_3)C{=}CH-$ chain of 3-ferrocenyl-2-crotonic acid $[NaOOCCH{=}(CH_3)CFc]$ can reduce the steric effects of the ferrocenyl group.[21f] This prompted us to further study the reaction of $NaOOCCH{=}(CH_3)CFc$ with other metal ions. In this paper, we present the synthesis, crystal structures, and electrochemical properties of two novel Zn(II) polymers, namely $[Zn\{\mu_2\text{-}OOCCH{=}(CH_3)CFc\}_2]_n$ (**1**) and $\{[Zn_2\{\mu_2\text{-}OOCCH{=}(CH_3)CFc\}_4(bpa)]\cdot 2MeOH\}_n$ [**2**, bpa = 1,2-bis(4-pyridyl) ethane]. Interestingly, polymer **2** is constructed from ferrocenyl carboxylate based paddle-wheel building units, $[Zn_2\{\mu_2\text{-}OOCCH{=}(CH_3)CFc\}_4]$. The tetrabridged dimeric cores are connected by organic bridging ligands, leading to a linear $[Zn_2\{\mu_2\text{-}OOCCH{=}(CH_3)CFc\}_4(bpa)]_n$ chain.

Results and discussion

Synthesis

It should be emphasized that the preparation of ferrocenyl carboxylate -containing coordination polymers from a mixture of $Zn(OAc)_2$ with ferrocenyl carboxylate and the bpa ligand should be carried out in the dark. In our recent papers,[21c,21f,23,24] we have given detailed explanations of why light should be excluded from the reaction mixture. The main reason is to avoid the photolysis in solution of the ferrocene derivatives, bearing photoactive groups. Therefore, crystals of **1** and **2** suitable for X-ray crystallography were grown by slow evaporation of their methanolic solutions in the dark. Both coordination polymers **1** and **2** are insoluble in common organic solvents, such as MeOH, EtOH, MeCN, acetone and THF, but soluble in highly polar solvents, such as DMSO or DMF. We have tried to determine the NMR and mass spectrometry data of the two polymers. Because of instrumental limitations, we could not obtain good signals for these two compounds. This may be due to the poor solubility and high molecular weights of the two polymers.

Interestingly, Zn(II) ions react with $NaOOCCH{=}(CH_3)CFc$ to give a linear chain $[Zn\{\mu_2\text{-}OOCCH{=}(CH_3)CFc\}_2]_n$ (**1**) in which the $FcC(CH_3){=}CHCOO^-$ anion acts as a bidentate bridging ligand. When both the organic ligand bpa and

† Electronic supplementary information (ESI) available: crystal packing view along the ***c*** axis of **1** and the DPVs of **1**, **2**, and the ferrocenyl ligand. See http://www.rsc.org/suppdata/nj/b4/b406983h/

DOI: 10.1039/b406983h

NaOOCCH=(CH$_3$)CFc react with Zn(II) ions, a novel polymer, {[Zn$_2${μ_2-OOCCH=(CH$_3$)CFc}$_4$(bpa)]·2MeOH}$_n$ (**2**), constructed with paddle-wheel building units is obtained. Four FcC(CH$_3$)=CHCOO$^-$ anions act as *O*,*O*′-bridging ligands, leading to a dimeric tetrabridged [Zn$_2${μ_2-OOCCH=(CH$_3$)CFc}$_4$] core. Obviously, bpa plays an important role in the structure of **2**, in other words, bpa incises the polymeric chain of **1**, forming a novel structure. From this point of view, bpa is a very useful ligand for the generation of novel polymers with mixed ferrocenyl and bipyridine ligands.

Crystal structure of [Zn{μ_2-OOCCH=(CH$_3$)CFc}$_2$]$_n$ (1)

This complex crystallizes in the orthorhombic space group *Pbcn*. Each Zn(II) ion is located at an inversion center and each FcC(CH$_3$)=CHCOO$^-$ anion acts as a bidentate ligand bridging the Zn(II) ions to form a one-dimensional infinite chain (Fig. 1).

The Zn(II) ion exhibits a slightly distorted tetrahedral conformation, being bound by the four oxygen atoms O1, O2A, O2C and O1B from four distinct FcC(CH$_3$)=CHCOO$^-$ units. The Zn–O bond distances are in the range of 1.943(3)–1.966(3) Å. The Zn–O distances are close to those of two related Zn(II) compounds with ferrocenyl carboxylate groups, for example, [Zn(μ_2-OOCFc)$_6$(μ_4-O)] [Zn–O 1.947(8)–2.048(10) Å][21e] and {[Zn(FcCOO)$_2$(bpt)]·2.5H$_2$O}$_n$ [bpt = *N*,*N*′-bis(3-pyridylmethyl)thiourea; Zn–O 1.946(4)–1.977(4) Å],[21e] but apparently shorter than those of the polymers [Zn(FcCOO)(η^2-FcCOO)(bbp)]$_n$ [bbp = 4,4′-trimethylenedipyridine; Zn–O 1.989(2)–2.387(2) Å][21e] and {[Zn(*o*-OOCC$_6$H$_4$COFc)$_2$(4,4′-bipy)(H$_2$O)$_2$]·2MeOH·2H$_2$O}$_n$ [4,4′-bipy = 4,4′-bipyridine; Zn–O 2.079(4)–2.150(4) Å].[21f] The bond angles around Zn1 fall between 102.4(1)° and 124.2(1)°, while the average bond angle at Zn1 is 109.2(1)°; the latter is close to 109.5° for an ideal tetrahedral structure.

It can be seen that two FcC(CH$_3$)=CHCOO$^-$ units bridge two neighboring Zn(II) ions in an *O*,*O*′-bridging mode to form an eight-membered ring. Each Zn(II) ion is coordinated by four ferrocenyl carboxylate ligands, so an infinite [Zn{μ_2-OOCCH=(CH$_3$)CFc}$_2$]$_n$ chain is formed. Viewed along the *c* axis, the [Zn{μ_2-OOCCH=(CH$_3$)CFc}$_2$]$_n$ chains pack with each other by intermolecular interactions. The distance of neighboring metallic cations Zn1···Zn1A in the chain is 3.760 Å, which is longer than that in the tetranuclear complexes [Zn(μ_2-OOCFc)$_6$(μ_4-O)] (3.1 Å) and (Zn$_4$O)(O$_2$CR)$_6$ (R = diethylamino, piperidino, or pyrrolidino; Zn···Zn distances being in the range 3.15 to 3.20 Å).[25] The intramolecular Zn1···Fe1, Zn1···Fe1A, Fe1···Fe1A, Fe1···Fe1B and Fe1···Fe1C distances are 6.455, 7.952, 6.592, 11.872 and 13.988 Å, respectively.

The average Fe–C$_{ring}$ distance of 2.039(4) Å in **1** is in good agreement with that of 2.04 Å for free ferrocene. The average C–C bond length and C–C–C angle of the cyclopentadienyl rings are 1.417(4) Å and 107.5(10)°, respectively, which are similar to those reported in the literature.[26] The cyclopentadienyl rings are perfectly planar and nearly parallel [a crystal packing view along the *c* axis of [Zn{μ_2-OOCCH=(CH$_3$)CFc}$_2$]$_n$ (**1**) is given as Fig. 3 in the Electronic supplementary information (ESI)].

Although a large number of Zn(II) coordination polymers with carboxylate ligands have been reported,[3] those containing carboxylate-substituted ferrocene derivatives only are rare. Duan *et al.* have described a novel ferrocene-based mixed-metal coordination polymer, NaZn$_3$L$_2$(OH)$_3$(H$_2$O) (H$_2$L = 1,1′-ferrocenedicarboxylic acid).[21d] Interestingly, our group has used two kinds of monosubstituted ferrocene carboxylate derivatives, HOOCFc and HOOCCH=(CH$_3$)CFc, to react with Zn(II) ion and has obtained two different products, namely the tetranuclear [Zn$_4$(μ_2-OOCFc)$_6$(μ_4-O)][21e] and the polymeric [Zn{μ_2-OOCCH=(CH$_3$)CFc}$_2$]$_n$, respectively. It is believed that the different carbon chain between the carboxylate and ferrocenyl groups yields the different molecular structures. The long –C(CH$_3$)C=CH– chain in **1** may allow the carboxylate group to bridge the metal ions to form a polymeric chain.

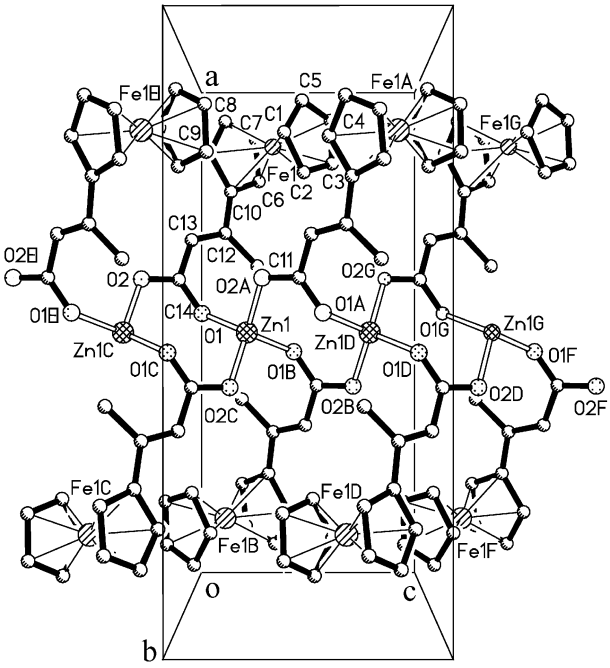

Fig. 1 1-D chain structure of [Zn(μ_2-OOCCH=(CH$_3$)CFc)$_2$]$_n$ (**1**). Symmetry transformations: A(x, 1 − y, 0.5 + z); B(1 − x, y, 0.5 − z); C(1 − x, 1 − y, −z); D(1 − x, 1 − y, 1, −z); E(x, 1 − y, z − 0.5); F(1 − x, y, 1.5 − z) and G(x, y, 1 + z).

Crystal structure of {[Zn$_2${μ_2-OOCCH=(CH$_3$)CFc}$_4$(bpa)]·2MeOH}$_n$ (2)

Compound **2** crystallizes in the space group *P*-1. The crystal structure of **2** consists of polymeric chains with each paddle-wheel building unit residing at an inversion center. The latter is connected by the centrosymmetric bpa ligand (Fig. 2). As shown in Fig. 2, four distinct FcC(CH$_3$)=CHCOO$^-$ ligands bridge two Zn(II) ions to form a paddle-wheel cage with Zn1···Zn1A = 2.928(9) Å and Zn–O distances in the range of 2.010(2)–2.095(2) Å. All the FcC(CH$_3$)=CHCOO$^-$ bridges in the dimeric cores exhibit a *syn–syn* geometry. Coordination of the nitrogen of bpa to the Zn(II) ion [Zn1–N1 distance of 2.047(2) Å] completes a square pyramidal coordination geometry around the metal center. The Zn···Zn distance in **2** is comparable to that of the related Zn(II) ferrocenyl dimer, [Zn$_2$(μ-OOCFc)$_4$(3-PyCOOCH$_3$)$_2$][24] [Zn···Zn = 2.934(11) Å], and of some other Zn(II) compounds constructed from paddle-wheel building units, such as [Zn(ndc)(3,4-lutidine)][27a] [ndc = 2,6-naphthalenedicarboxylic acid; Zn···Zn = 2.934(11) Å], [Zn$_2$(C$_4$H$_5$O$_2$)$_4$(C$_6$H$_4$N$_2$)$_2$][27b] (Zn···Zn = 2.910 Å), and Zn(BDC)·(DMF)(H$_2$O)[27c] [BDC = 1,4-benzenedicarboxylate; Zn···Zn = 2.940(3) Å].

The Zn atom in **2** is located at 0.1149 Å above the O1–O3–O2A–O4A basal plane. The maximum deviation of the oxygen atom from the mean plane is 0.0001 Å. The Zn–N distance is similar or slightly shorter than those found in several related coordination polymers, such as {[Zn(fca)$_2$(bpe)]·2H$_2$O}$_n$ [Zn–N 2.196(8)–2.205(8) Å],[21c] {[Zn(OOCFc)$_2$(bpt)]·2.5H$_2$O}$_n$ [Zn–N 2.036(4)–2.077(4) Å],[21e] [Zn(OOCFc)(η^2-OOCFc)(bbp)]$_n$ [Zn–N 2.103(2)–2.108(2) Å],[21e] and {[Zn(*o*-OOCC$_6$H$_4$COFc)$_2$(4,4′-bipy)(H$_2$O)$_2$]·2MeOH,2H$_2$O}$_n$ [Zn–N 2.142(7)–2.218(7) Å].[21f] The two pyridyl rings of the bpa ligands are parallel with each other with a dihedral angle of 0°, which is

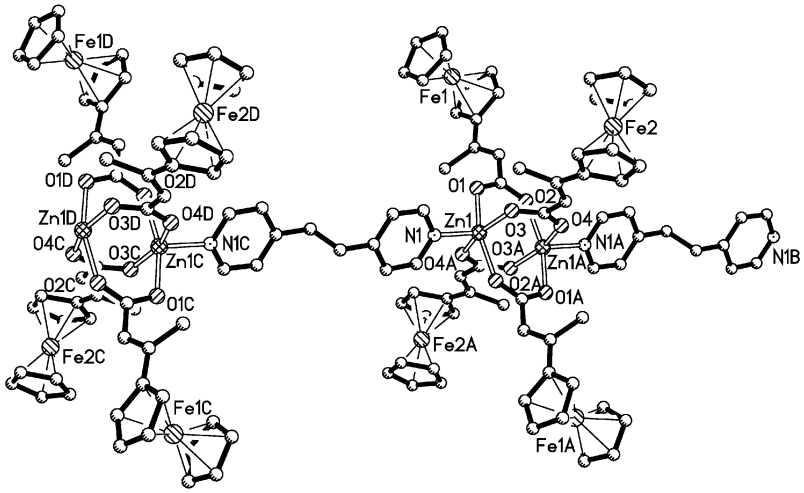

Fig. 2 1-D chain of $\{[Zn_2(\mu_2\text{-}OOCCH{=}(CH_3)CFc)_4(bpa)]\cdot 2MeOH\}_n$ (**2**) containing paddle-wheel building units. Symmetry transformations: A($-x$, $1-y$, $1-z$); B($1+x$, $y-1$, z); C($-1-x$, $2-y$, $1-z$) and D($x-1.5$, $1+y$, z).

significantly different from that of the polymer $\{[Zn(o\text{-}OOCC_6H_4COFc)_2(4,4'\text{-bipy})(H_2O)_2]\cdot 2MeOH,2H_2O\}_n$ (the dihedral angle of the two pyridyl rings being 83.1°).[21f] The bpa ligands connect the $[Zn_2\{\mu_2\text{-}OOCCH{=}(CH_3)CFc\}_4]$ cores more tightly to form a linear chain. In addition, the bond lengths and angles within the ferrocenyl group are unexceptional and similar to those reported in the literature.[26]

Although a few dimeric compounds[24,27] and polymeric compounds that contain the paddle-wheel building units have been reported,[3,28] most of these studies focused on benzene-based carboxylate derivatives. To the best of our knowledge, there are no reports on Zn(II) polymers constructed of ferrocenyl carboxylate based paddle-wheel units. Our compound is the first example of a Zn(II) coordination polymer with ferrocene-containing paddle-wheel units and the organic bpa ligands.

IR spectroscopy

According to previous reports in the literature,[26,29] the characteristic IR bands of the ferrocenyl group at 3097 and 489 cm^{-1} can be attributed to ν(C–H) and ν(Fe–Cp) vibrations, respectively. Similar values were found in the two polymers (3091 and 481 cm^{-1} for **1**; 3093 and 509 cm^{-1} for **2**). The strong absorption bands at 1616 and 1504 cm^{-1} for **1** (1626 and 1528 cm^{-1} for **2**) are assigned to the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ vibrations, respectively. The vibrational bands around 1335 and 1030 cm^{-1} for **1** (1335 and 1033 cm^{-1} for **2**) can be attributed to the $\delta(CH_3)$ and $\rho(CH_3)$, respectively.[30] In the middle energy range, the strong absorption band around 1630 cm^{-1} can be assigned to the ν(C=O) vibration. In conclusion, these IR data are consistent with the crystal data of the two compounds.

Redox properties

Recently, much attention has been devoted to the chemistry of ferrocenyl complexes because of the high thermal stability and electrochemical properties of ferrocene.[31] As two or more ferrocenyl fragments are connected to form new compounds, further interesting applications can be envisaged, for example, drawing on intermetallic electronic communication, and many studies have been reported regarding intramolecular electron-exchange reactions.[32] Thus, we have studied the electrochemical properties of polymers **1** and **2**.

Differential pulse voltammograms of the two polymers and of the ferrocenyl ligand, NaOOC–CH=(CH_3)CFc were determined in DMF solution. It is to be pointed that our group has determined the molecular weights of several ferrocene carboxylate containing coordination polymers in DMF solution[33] and found that these are high; that is to say, these polymers show some stability in DMF solution. We believe that the similar polymers **1** and **2** are also stable in DMF solution. All of the compounds showed single peaks with a half-wave potential at 0.560 V for **1**, 0.560 V for **2** and 0.565 V for NaOOCCH=(CH_3)CFc. [The differential pulse voltammograms of polymers **1**, **2**, and the ferrocenyl ligand, NaOOCCH=(CH_3)CFc, are given in the ESI.] Obviously, these observed redox peaks correspond to the redox processes of the ferrocenyl moieties.[34] No electronic communication among the different ferrocenyl subunits was observed in the electrochemical data. Moreover, the half-wave potential of the ferrocenyl moieties seems to be uninfluenced by the Zn(II) ions in the two polymers; similar behavior can be found in the related polymer $\{[Pb\{\mu_2\text{-}\eta^2\text{-}OOCCH{=}(CH_3)CFc\}_2]\cdot MeOH\}_n$[21f] and $[BaL(H_2O)]_n$ (H_2L = 1,1′-ferrocenedicarboxylic acid).[34] However, this conclusion is in contradiction with what has been observed in several other ferrocenyl polymers, for example, the metal ions Zn(II), Cd(II) and Pb(II) in the polymers $\{[Zn(o\text{-}OOCC_6H_4COFc)_2(4,4'\text{-bipy})(H_2O)_2]\cdot 2MeOH\cdot 2H_2O\}_n$, $\{[Cd(o\text{-}OOCC_6H_4COFc)_2(bpe)(MeOH)_2]\cdot 2H_2O\}_n$, and $[Pb(o\text{-}OOCC_6H_4COFc)(\eta^2\text{-}o\text{-}OOCC_6H_4COFc)(bpe)]_n$[21f] have some influence on the half-wave potential of the ferrocenyl moieties, consistent with the results of other groups on transition metal ferrocenyl system.[21a,35]

Conclusions

By reaction of either ferrocenyl-substituted carboxylate or both ferrocenyl carboxylate and bipyridine-based ligands with metal ions in the dark and under mild conditions, two crystalline products have been successfully prepared. The X-ray diffraction results indicate that both the compounds are novel 1-D ferrocene-containing coordination polymers. In particular, one polymer is constructed from ferrocene-based paddle-wheel building units. The IR data are consistent with the X-ray analysis results. In addition, the electrochemical studies reveal that the half-wave potential of the ferrocenyl moieties seems to be uninfluenced by the Zn(II) ions in the two polymers.

Experimental

General Details

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. 3-Ferrocenyl-2-crotonic acid [HOOC–CH=(CH_3)CFc] was

Table 1 Crystallographic data for **1** and **2**

Compound	**1**	**2**
Formula	$C_{28}H_{26}Fe_2O_4Zn$	$C_{35}H_{36}Fe_2NO_5Zn$
FW	603.56	727.72
Crystal system	Orthorhombic	Triclinic
Space group	*Pbcn*	*P*-1
a/Å	16.836(3)	8.0243(16)
b/Å	19.452(4)	12.953(3)
c/Å	7.4853(15)	15.781(3)
α/°	90	95.61(3)
β/°	90	104.30(3)
γ/°	90	98.47(3)
U/Å^3	2451.5(9)	1556.7(5)
D_c/Mg m^{-3}	1.635	1.553
Z	4	2
μ/mm^{-1}	2.171	1.728
Collected reflect.	5233	5118
Unique reflect.	1691	5118
R_{int}	0.1089	0.0000
R^a	0.0380	0.0339
$R_w{}^b$	0.0728	0.0611

^{a} $R = \sum \| F_o \| - \| F_c \| / \sum | F_o |$. ^{b} $R_w = [\sum (\| F_o \| - \| F_c \|)^2 / \sum w | F_o |^2]^{\frac{1}{2}}$

prepared according to a literature method.[36] Its sodium salt was prepared by the reaction with sodium methoxide.

C, H and N analyses were carried out on a MOD 1106 analyzer. IR data were recorded on a Bruker TENSOR 27 spectrophotometer with KBr pellets in the 400–4000 cm^{-1} region. Differential pulse voltammograms were recorded with a CHI650 electrochemical analyzer utilizing a three-electrode configuration of a Pt working electrode, a Pt auxiliary electrode, and a commercially available saturated calomel electrode as the reference electrode with pure N_2 gas inlet and outlet. The measurements were performed in DMF solution that contained tetra-*n*-butylammonium perchlorate (*n*-Bu_4NClO_4, 0.1 mol dm^{-3}) as supporting electrolyte with a 50 ms pulse width and a 20 ms sample width. The potentials were scanned from +0.2 to +1.0 V at a scan rate of 20 mV s^{-1}.

Syntheses

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.*

$[Zn\{\mu_2$-OOCCH=(CH_3)CFc$\}_2]_n$ (1). NaOOCCH=(CH_3)CFc (29.2 mg; 0.10 mmol) in MeOH (5 ml) was added dropwise to a methanol solution (6 ml) of $Zn(OAc)_2 \cdot 2H_2O$ (11.8 mg; 0.05 mmol). The resulting solution was allowed to stand at room temperature in the dark. Good quality red crystals were obtained after two weeks. Crystals of **1** are stable in air. Yield: 57%. Anal. calcd for $C_{28}H_{26}Fe_2O_4Zn$: C, 55.67; H, 4.31%; found: C, 55.58; H, 4.21%. IR (cm^{-1}, KBr): 3429 m, 3091 m, 1616 s, 1504 s, 1414 s, 1335 m, 1258 s, 1105 m, 1030 m, 941 m, 817 m, 684 m, 514 m, 481 m.

$\{[Zn_2\{\mu_2$-OOCCH=(CH_3)CFc$\}_4$(bpa)$] \cdot 2$MeOH$\}_n$ (2). NaOOCCH=(CH_3)CFc (29.2 mg; 0.10 mmol) and bpa (9.1 mg, 0.05 mmol) were dissolved in 10 ml of MeOH. A solution of $Zn(Ac)_2 \cdot 2H_2O$ (11.8 mg; 0.05 mmol) in MeOH (5 ml) was added dropwise to the above mixture. The resulting orange solution was allowed to stand at room temperature in the dark. Good quality red crystals of **2** were obtained after two weeks. Yield: 61%. Anal. calcd for $C_{35}H_{36}Fe_2NO_5Zn$: N, 1.90; C, 57.71; H, 4.95%; found: N, 1.92; C, 57.41; H, 4.55%. IR (cm^{-1}, KBr): 3329 m, 3093 m, 2936 m, 1626 s, 1528 s, 1412 s, 1335 m, 1257 s, 1106 m, 1033 m, 938 m, 819 m, 673 m, 509 m.

Table 2 Selected bond distances (Å) and angles (deg) for **1** and **2**

Polymer 1[a]			
Zn(1)–O(2)A	1.943(3)	Zn(1)–O(2)C	1.943(3)
Zn(1)–O(1)B	1.966(3)	O(1)–C(14)	1.266(5)
Zn(1)–O(1)	1.966(3)	C(13)–C(14)	1.462(5)
C(12)–C(13)	1.344(5)	O(2)–C(14)	1.272(4)
O(2)A–Zn(1)–O(2)C	124.20(19)	O(2)A–Zn(1)–O(1)	102.39(12)
O(2)A–Zn(1)–O(1)B	111.29(11)	O(2)C–Zn(1)–O(1)B	102.39(12)
C(14)–O(1)–Zn(1)	129.2(3)	C(14)–O(2)–Zn(1)C	116.1(3)
C(10)–C(12)–C(11)	116.2(3)	C(12)–C(13)–C(14)	128.9(3)
O(1)–C(14)–C(13)	123.8(3)	O(2)–C(14)–C(13)	115.1(3)
C(14)–O(2)–Zn(1)C	116.1(3)	O(2)C–Zn(1)–O(1)	111.29(11)
O(1)–Zn(1)–O(1)B	103.75(16)	O(1)–C(14)–O(2)	121.1(4)
C(13)–C(12)–C(11)	124.7(4)	C(14)–O(1)–Zn(1)	129.2(3)
Polymer 2[b]			
Zn(1)–O(1)	2.079(2)	Zn(1)–O(3)	2.010(2)
Zn(1)–O(4)A	2.015(2)	Zn(1)–N(1)	2.047(2)
O(1)–C(14)	1.270(3)	Zn(1)–O(2)A	2.095(2)
O(4)–C(28)	1.265(3)	O(2)–C(14)	1.250(3)
C(26)–C(27)	1.333(4)	C(12)–C(13)	1.331(4)
C(13)–C(14)	1.480(4)	C(27)–C(28)	1.464(5)
O(3)–C(28)	1.264(3)		
O(1)–Zn(1)–O(2) A	160.08(8)	O(2)A–Zn(1)–N(1)	93.46(9)
O(1)–Zn(1)–N(1)	106.27(9)	O(1)–Zn(1)–O(4)A	85.79(10)
O(1)–Zn(1)–O(3)	89.33(10)	O(2)A–Zn(1)–O(3)	89.23(10)
O(4)A–Zn(1)–O(3)	159.40(8)	N(1)–Zn(1)–O(3)	102.09(10)
O(2)A–Zn(1)–O(4)A	88.61(10)	O(3)–C(28)–O(4)	123.7(3)
N(1)–Zn(1)–O(4)A	98.49(10)	O(1)–C(14)–O(2)	123.3(3)

[a] Symmetry transformations used to generate equivalent atoms: A = x, $-y+1$, $z+1/2$; B = $-x+1$, y, $-z+1/2$; C = $-x+1$, $-y+1$, $-z$. [b] Symmetry transformations used to generate equivalent atoms: A = $-x$, $-y+1$, $-z+1$.

X-Ray crystallography

Crystal data and experimental details for compounds **1** and **2** are collected in Table 1.‡ All measurements were made on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated MoKα radiation (λ = 0.710 73 Å). Red prismatic single crystals of **1** (0.23 × 0.20 × 0.20 mm^3) and **2** (0.22 × 0.20 × 0.19 mm^3) were selected and mounted on a glass fiber. All data were collected at a temperature of 291(2) K using the $\omega - 2\theta$ scan technique. A correction for secondary extinction was applied.

The two structures were solved by direct methods and expanded using the Fourier technique. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were inserted at the calculated positions and allowed to ride on their respective parent atoms. All calculations were performed using the SHELX-97 crystallographic software package.[37] Selected bond lengths and bond angles are listed in Table 2.

Acknowledgements

The authors thank the National Natural Science Foundation of China (Nos. 20001006 and 20371042), the Excellent Young Teachers Program In Higher Education Institute, and the Henan Province for financial support.

References

1 C. Janiak, *Dalton Trans.*, 2003, 2781 and references cited therein.
2 J. Y. Lu, *Coord. Chem. Rev.*, 2003, **246**, 327 and references cited therein.
3 A. Erxleben, *Coord. Chem. Rev.*, 2003, **246**, 203 and references cited therein.

‡ CCDC reference numbers 256288 and 256319. See http://www.rsc.org/suppdata/nj/b4/b406983h/ for crystallographic data in .cif or other electronic format.

4 B. Moulton and M. J. Zaworotko, *Curr. Opin. Solid State Mater. Sci.*, 2002, **6**, 117 and references cited therein.
5 S. R. Batten, *Curr. Opin. Solid State Mater. Sci.*, 2001, **5**, 107 and references cited therein.
6 J. P. H. Charmant, A. H. M. Monowar Jahan, N. C. Norman, A. G. Orpen and T. J. Podesta, *CrystEngComm*, 2004, **6**, 29.
7 A. N. Khlobystov, A. J. Blake, N. R. Champness, D. A. Lemenovskii, A. G. Majouga, N. V. Zyk and M. Schroder, *Coord. Chem. Rev.*, 2001, **222**, 155 and references cited therein.
8 R. J. Puddephatt, *Coord. Chem. Rev.*, 2001, **216–217**, 313 and references cited therein.
9 R. Robson, *J. Chem. Soc., Dalton Trans.*, 2000, 3735 and references cited therein.
10 G. F. Swiegers and T. J. Malefetse, *Chem. Rev.*, 2000, **100**, 3483 and references cited therein.
11 T. Kaliyappan and P. Kannan, *Prog. Polym. Sci.*, 2000, **25**, 343 and references cited therein.
12 P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 2639 and references cited therein.
13 M. Rehahn, *Mater. Sci. Technol.*, 1999, **20**, 319 and references cited therein.
14 S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460 and references cited therein.
15 D. Venkataraman, G. F. Gardner, S. Lee and J. S. Moore, *J. Am. Chem. Soc.*, 1995, **117**, 11600.
16 (*a*) S.-I. Noro, S. Kitagawa, M. Kondo and K. Seki, *Angew. Chem., Int. Ed.*, 2000, **39**, 2081; (*b*) T. Okubo, S. Kitagawa, M. Kondo, H. Matsuzaka and T. Ishii, *Angew. Chem., Int. Ed.*, 1999, **38**, 931; (*c*) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; (*d*) S. Leininger, B. Olenyuk and J. Stang, *Chem. Rev.*, 2000, **100**, 853; (*e*) M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417.
17 (*a*) C. Chen and K. S. Suslick, *Coord. Chem. Rev.*, 1993, **128**, 293; (*b*) Z. F. Chen, R. G. Xiong, B. F. Abrahams, X. Z. You and C. M. Che, *J. Chem. Soc., Dalton Trans.*, 2001, 2453; (*c*) H. W. Hou, Y. L. Wei, Y. L. Song, Y. Zhu, L. K. Li and Y. T. Fan, *J. Mater. Chem.*, 2002, 838; (*d*) H. W. Hou, Y. L. Song, H. Xu, Y. L. Wei, Y. T. Fan, Y. Zhu, L. K. Li and C. X. Du, *Macromolecules*, 2003, **36**, 999; (*e*) H. W. Hou, X. R. Meng, Y. L. Song, Y. T. Fan, Y. Zhu, H. J. Lu, C. X. Du and W. H. Shao, *Inorg. Chem.*, 2002, **41**, 4068; (*f*) X. R. Meng, Y. L. Song, H. W. Hou, Y. T. Fan, G. Li and Y. Zhu, *Inorg. Chem.*, 2003, **42**, 1306.
18 (*a*) W. Fujita and K. Awaga, *J. Am. Chem. Soc.*, 2001, **123**, 3601; (*b*) F. Lloret, G. D. Munno, M. Julve, J. Cane, R. Ruiz and A. Caneschi, *Angew. Chem., Int. Ed.*, 1998, **37**, 135; (*c*) J. A. Real, E. Andres, M. C. Munoz, M. Julve, I. Granier, A. Bousseksou and F. Varret, *Science*, 1995, **268**, 265.
19 K. Maruoka, N. Murase and H. Yamamoto, *J. Org. Chem.*, 1993, **58**, 2938.
20 B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **112**, 1546.
21 (*a*) R. Horikoshi, T. Mochida and H. Moriyama, *Inorg. Chem.*, 2002, **41**, 3017; (*b*) R. Horikoshi, M. Ueda and T. Mochida, *New J. Chem.*, 2003, **27**, 933; (*c*) G. Li, H. W. Hou, Y. Zhu, X. R. Meng, L. W. Mi and Y. T. Fan, *Inorg. Chem. Commun.*, 2002, **5**, 929; (*d*) D. Guo, C. Y. Duan, F. Lu and Q. J. Meng, *J. Chem. Soc., Dalton Trans.*, 2002, 2593; (*e*) H. W. Hou, L. K. Li, G. Li, Y. T. Fan and Y. Zhu, *Inorg. Chem.*, 2003, **42**, 3501; (*f*) G. Li, H. W. Hou, L. K. Li, X. R. Meng, Y. T. Fan and Y. Zhu, *Inorg. Chem.*, 2003, **42**, 4995.
22 (*a*) H. Plenio and C. Aberle, *Chem.-Eur. J.*, 2001, **7**, 4438; (*b*) A. Togni and T. Hayashi, *Ferrocenes: Homogenous Catalysis, Organic Synthesis, Materials Science*, VCH Publishers, New York, 1995; (*c*) B. Bildstein, M. Schweiger, H. Angleitner, H. Kopacka, K. Wurst, K. H. Ongania, M. Fontani and P. Zanello, *Organometallics*, 1999, **18**, 4286; (*d*) G. Li, Y. L. Song, H. W. Hou, L. K. Li, Y. T. Fan, Y. Zhu, X. R. Meng and L. W. Mi, *Inorg. Chem.*, 2003, **42**, 913; (*e*) S. Barlow, H. E. Bunting, C. Ringham, J. C. Green, G. U. Bublitz, S. G. Boxer, J. W. Perry and S. R. Marder, *J. Am. Chem. Soc.*, 1999, **121**, 3715; (*f*) H. Plenio, C. Aberle, Y. A. Shihadeh, J. M. Lloris, R. Martínez-Máñez, T. Pardo and J. Soto, *Chem.-Eur. J.*, 2001, **7**, 2848.
23 H. W. Hou, G. Li, L. K. Li, Y. Zhu, X. R. Meng and Y. T. Fan, *Inorg. Chem.*, 2003, **42**, 428.
24 G. Li., B. Y. Chen, L. K. Li, H. W. Hou, Y. Zhu and Y. T. Fan, *J. Coord. Chem.*, 2003, **56**, 877.
25 C. S. McCowan, T. L. Groy and M. T. Caudle, *Inorg. Chem.*, 2002, **41**, 1120.
26 (*a*) E. R. Lippincott and R. D. Nelson, *Spectrochim. Acta*, 1958, **10**, 307; (*b*) F. Takusagawa and T. F. Koetzle, *Acta Crystallogr., Sect. B*, 1979, **35**, 2888.
27 (*a*) K. O. Kongshaug and H. Fjellvåk, *J. Solid. State Chem.*, 2002, **166**, 213; (*b*) W. Clegg, P. A. Hunt and B. P. Straughan, *Acta Crystallogr., Sect. C*, 1995, **51**, 613; (*c*) H. Li, M. Eddaoudi, T. L. Groy and O. M. Yaghi, *J. Am. Chem. Soc.*, 1998, **120**, 8571; (*d*) B. Singh, J. R. Long, F. F. Biani, D. Gatteschi and P. Staropoulos, *J. Am. Chem. Soc.*, 1997, **119**, 7030; (*e*) W. Clegg, I. R. Little and B. P. Straughan, *J. Chem. Soc., Dalton Trans.*, 1986, 1283; (*f*) Q. D. Zhou, T. W. Hambley, B. J. Kennedy, P. A. Lay, P. Turner, B. Warwick, J. R. Biffin and H. L. Regtop, *Inorg. Chem.*, 2000, **39**, 3742; (*g*) V. Zelenak, M. Sabo, W. Massa and J. Cernak, *Acta Crystallogr., Sect. C*, 2004, **60**, m85.
28 (*a*) J. Tao, X. Yin, R. B. Huang, L. S. Zheng and S. Weng Ng, *Inorg. Chem. Commun.*, 2002, **5**, 975; (*b*) M. E. Braun, C. D. Steffek, J. Kim, P. G. Rasmussen and O. M. Yaghi, *Chem. Commun.*, 2001, 2532.
29 F. A. Cotton, L. R. Fallvello, A. H. Reid and J. H. Tocher, *J. Organomet. Chem.*, 1987, **319**, 87.
30 F. Ribot, P. Toledano and C. Sanchez, *Inorg. Chim. Acta*, 1991, **185**, 239.
31 (*a*) A. Togni and T. Hayashi, *Ferrocenes*, VCH, , Weinheim, Germany, 1995; (*b*) N. J. Long, *Metallocenes*, Blackwell Science, Ltd., London, 1st edn., 1997.
32 J. A. Mata and E. Peris, *J. Chem. Soc., Dalton Trans.*, 2001, 3634 and references cited therein.
33 H. W. Hou, L. K. Li, Y. Zhu, Y. T. Fan and Y. Q. Qiao, *Inorg. Chem.*, 2004, **43**, 4767.
34 D. Guo, B. G. Zhang, C. Y. Duan, X. Cao and Q. J. Meng, *J. Chem. Soc., Dalton Trans.*, 2003, 282.
35 (*a*) S. S. Sun, J. A. Anspach and A. J. Lees, *Inorg. Chem.*, 2002, **41**, 1862; (*b*) T. Morikita and T. Yamamoto, *J. Organomet. Chem.*, 2001, **637–639**, 809; (*c*) A. Ion, M. Buda, J. C. Moutet, E. Saint-Aman, G. Royal, I. Gautier-Luneau, M. Bonin and R. Ziessel, *Eur. J. Inorg. Chem.*, 2002, 1357.
36 Q. B. Liao, M. G. Liu, K. F. Tong, G. F. Luo, Z. D. Shi and B. L. Chen, *Huaxue Yanjiu Yu Yingyong*, 2002, **3**, 255 (in Chinese).
37 G. M. Sheldrick, *SHELX-97, Program for the Solution and Refinement of Crystal Structures*, University of Göttingen, Germany, 1997.