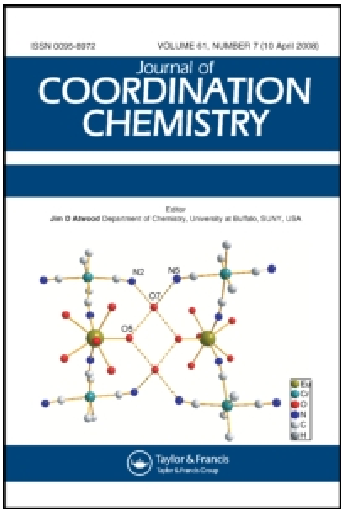

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Synthesis, structure and electrochemical properties of a zinc(II) coordination polymer based on ferrocenyl-substituted carboxylate and <i>bis</i>(benzimidazolyl)pentane ligands

Gang Li[a]; Zi-Feng Li[a]; Jing-Xia Wu[a]; Chun Yue[a]; Hong-Wei Hou[a]
[a] Department of Chemistry, Zhengzhou University, Zhengzhou, P. R. China

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Synthesis, structure and electrochemical properties of a zinc(II) coordination polymer based on ferrocenyl-substituted carboxylate and *bis*(benzimidazolyl)pentane ligands

GANG LI*, ZI-FENG LI, JING-XIA WU, CHUN YUE and HONG-WEI HOU

Department of Chemistry, Zhengzhou University, Zhengzhou 450052, P. R. China

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By reaction of two ligands, Na(*o*-$OOCC_6H_4COFc$) (Fc = (η^5–C_5H_5)Fe(η^5–C_5H_4)) and 1,1′–(1,5–pentamethylene)*bis*-1*H*-benzimidazole (pbbm), with $Zn(OAc)_2 \cdot 2H_2O$ in methanol solution, we have synthesized a zinc(II) coordination polymer [Zn(*o*-$OOCC_6H_4COFc)_2$(pbbm)]$_n$. The polymer was characterized by X-ray single crystal diffraction, IR spectroscopy, and elemental analysis. Each Zn atom was connected by two pbbm ligands, leading to an infinite one-dimensional chain. Two monodentate *o*-$FcCOC_6H_4COO^-$ anions completed the coordination sphere of the central Zn(II) ion. The polymer's electrochemical properties were investigated in DMF solution.

Keywords: Zinc(II); Crystal structure; Coordination polymer; Ferrocene-based carboxylate; Electrochemical properties

1. Introduction

Ferrocene-based carboxylate compounds have been exploited as multifunctional ligands due to diversity of their binding modes, terminal monodentate, chelating to one metal center, bridging bidentate and bridging tridentate and a large number of mononuclear complexes containing ferrocene-based carboxylate components have been described [1]; however, coordination polymers bearing ferrocene-based carboxylate ligands are limited [2]. A few coordination polymers with ferrocenecarboxylato [2a–2c, 2h] and 1,1′-ferrocenedicarboxylato ligand [2d–2f] have been reported.

Our group has prepared several coordination polymers constructed from metal derivatives of *o*-ferrocenoylbenzoic acid (*o*-$HOOCC_6H_4COFc$) [2i] or 3-ferrocenyl-2-crotonic acid (HOOC–CH=C(CH_3)Fc) [2i, 2j], and determined their electrochemical properties.

Our studies of ferrocene carboxylato-containing polymer formation [2h, 2i, 2j] have shown that ligands containing two pyridyl moieties, such as 4,4′-bipyridine (4,4′-bipy), 1, 2-*bis*(4-pyridyl)ethane (bpe), *N*, *N*′-*bis*(3-pyridylmethyl)thiourea (bpt), and 1, 3-*bis*(4-pyridyl)propane (bbp), facilitated formation of ferrocenyl-substituted

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*Corresponding author. Email: gangli@zzu.edu.cn

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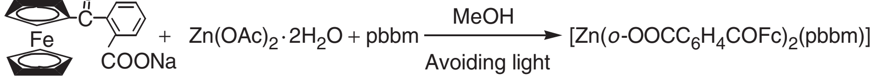
carboxylate polymers. Ferrocenoyl carboxylate, with its bulky ferrocenyl and phenyl substituents and three oxygen atoms of carboxylate and carbonyl groups, has the potential to coordinate several metal ions simultaneously. However, there are no reports about coordination polymers consisting only of *o*-$FcCOC_6H_4COO^-$ anions and metal cations [3]. Only when 4,4′-bipy or bpe were added could polymers containing the *o*-$FcCOC_6H_4COO^-$ ligands be formed [2i]. Three polymers containing both *o*-$FcCOC_6H4COO^-$ anions and neutral organic bridging ligands have been reported [2i]. Our target is to prepare more coordination polymers containing *o*-$FcCOC_6H_4COO^-$ units and determine their crystal structures. The organic bridging ligand used here is 1,1′-(1, 5-pentamethylene)*bis*-1*H*-benzimidazole (pbbm), a very useful multi-dentate bridging ligand due to its $–CH_2–CH_2–CH_2–CH_2–CH_2–$ and *bis*-benzimidazole units. For instance, one-dimensional cup-like helical chains $\{[Co(NO_3)(pbbm)_2]NO_3 \cdot 1/2H_2O\}_n$ and $\{[CdCl(pbbm)_2]Cl \cdot CH_3OH\}_n$, and a one-dimensional wave-like linear chain $\{[Cu(OOCCH_3)_2(pbbm)] \cdot CH_3OH\}_n$ [4], have been built from pbbm and metal ions.

In this article, we report the reaction of Na(*o*-$OOCC_6H_4COFc$) with $Zn(OAc)_2 \cdot 2H_2O$ in the presence of pbbm (scheme 1), which afforded a wave-like single chain zinc(II) coordination polymer $[Zn(o\text{-}OOCC_6H_4COFc)_2(pbbm)]_n$, and investigated the polymer's electrochemical properties.



Scheme 1. The reaction process of the polymer $[Zn(o\text{-}OOCC_6H_4COFc)_2(pbbm)]_n$.

2. Experimental

2.1. *Materials and physical techniques*

All chemicals were of reagent grade obtained from commercial sources and used without further purification. Sodium *o*-ferrocenoylbenzoate [5] and pbbm [6] were prepared according to literature methods.

IR spectra were recorded on a Nicolet NEXUS 470-FTIR spectrophotometer as KBr pellets in the 400–4000 cm^{-1} region. Elemental analyses (EA) (C, H and N) were carried out on a FLASH EA1112 Elemental Analyzer. The molecular weight and molecular weight distribution of the polymer were determined at 40°C by gel permeation chromatography (Waters associates model HPLC/GPC 515 liquid chromatograph, equipped with a refractive index detector and μ-Styragel columns and calibrated with standard polystyrene), using DMF as the eluent and a flow rate of 1.0 mL min^{-1}. Differential pulse voltammetry (DPV) studies were performed with a CHI650 electrochemical analyzer utilizing the three-electrode configuration of a vitreous carbon 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 tetrabutyl ammonium perchlorate ($[Bu_4N][ClO_4]$) (0.1 mol L^{-1}) as supporting electrolyte. DPV curves were recorded at a 20 mV s^{-1} scan rate with pulse width of 50 ms and sample width of 16.7 ms. The potential was scanned from +0.2 to +0.8 V. Potentials in this paper are given versus the ferrocene/ferrocenium couple.

2.2. *Preparation of [Zn(o-OOCC$_6$H$_4$COFc)$_2$(pbbm)]$_n$*

Pbbm (7.8 mg, 0.05 mmol) and Na(*o*-OOCC$_6$H$_4$COFc) (33.5 mg, 0.1 mmol) were dissolved separately and then mixed producing 7 mL of methanol solution. This solution was added slowly dropwise to a solution of Zn(OAc)$_2\cdot$2H$_2$O (11.0 mg; 0.05 mmol) in 5 mL of methanol. The red solution was filtered and allowed to stand at room temperature in the dark. Good quality red crystals were obtained after one month. Yield: 48%. Decomposition temperature: 225°C. Anal. Calcd for $C_{55}H_{46}Fe_2N_4O_6Zn$ (%): C, 61.57; H, 4.34; N, 5.52. Found: C, 61.38; H, 4.42; N, 5.68. IR (KBr, cm^{-1}): 3453m, 3109m, 1652m, 1614m, 1589m, 1563m, 1511w, 1465m, 1375m, 1293m, 750m, 717m, 510m, 485m.

2.3. *Crystallography*

A red single crystal of [Zn(*o*-OOCC$_6$H$_4$COFc)$_2$(pbbm)]$_n$ ($0.23 \times 0.14 \times 0.11$ mm^3) was selected and mounted on a glass fiber. All measurements were made on a Bruker Smart 1000 diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). All data were collected at 291(2) K using the ω–2θ scan mode and corrected for Lorenz-polarization effects. A total of 35520 reflections in the range of $2.30 \le \theta \le 25.50°$ ($-34 \le h \le 34$, $-21 \le k \le 21$, $-24 \le l \le 24$) and 8699 unique ones ($R_{\mathrm{int}} = 0.0831$) were collected. Empirical absorption corrections by SADABS were carried out.

The structure was solved by direct methods and expanded by the Fourier technique. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms bound to carbon were calculated theoretically. The final cycle of full-matrix least- squares refinement was based on 4853 observed reflections and 613 variable parameters to give the final $R = 0.0621$ and $wR = 0.1659$ ($I > 2\sigma(I)$). The goodness-of-fit indicator is 1.016. The maximum peak in the final difference Fourier map is 0.398 e Å^{-3} and the minimum −0.317 e Å^{-3}. All calculations were performed with SHELX-97 crystallographic software [7].

3. Results and discussion

3.1. *Synthesis*

In order to prepare metal-organic polymers we first studied the reaction of sodium ferrocenoylcarboxylate with metal salts without added organic bridging ligands. Several metal acetates (for example, Zn(OAc)$_2\cdot$2H$_2$O, Cd(OAc)$_2\cdot$2H$_2$O or Pb(OAc)$_2\cdot$3H$_2$O) have been treated with Na(*o*-OOCC$_6$H$_4$COFc) in methanol solution by a method similar to that used to prepare [Zn(*o*-OOCC$_6$H$_4$COFc)$_2$(pbbm)]$_n$, but without added pbbm. The mixture of Na(*o*-OOCC$_6$H$_4$COFc) and a metal acetate was put aside in the dark. The orange-red precipitates were collected after several weeks and analyzed by EA and IR spectroscopy. The results of analyses indicated that the precipitates were mononuclear complexes. X-Ray quality crystals of these complexes could not be grown. Because our target compounds are coordination polymers containing ferrocene groups, no further attempts have been made to prepare polymers containing only *o*-FcCOC$_6$H$_4$COO- anions and metal cations. Taking into account structural characteristics (relatively large separation, or flexible properties) of the organic bridging ligands, such as 4,4′-bipy, bpe and pbbm, we suppose that these ligands reduce the steric effect of *o*-FcCOC$_6$H$_4$COO$^-$ anions, and thus facilitate the introduction of the ferrocenyl group to polymers. The successful preparation of the polymers, {[Zn(*o*-OOCC$_6$H$_4$COFc)2(4,4′-bipy)(H$_2$O)$_2$] · 2CH$_3$OH · 2H$_2$O}$_n$, {[Cd(*o*-OOCC$_6$H$_4$COFc)$_2$(bpe)(CH$_3$OH)$_2$] · 2H$_2$O}$_n$, [Pb(*o*-OOCC$_6$H4COFc)(η^2-*o*-OOCC$_6$H$_4$COFc)(bpe)]$_n$ [2i] and [Zn(*o*-OOCC$_6$H$_4$COFc)$_2$(pbbm)]$_n$ confirms our synthetic strategy. These organic bridging ligands are effective compounds for the preparation of coordination polymers with ferrocenyl groups.

Another key for the coordination polymer preparation is that mixing Na(*o*-OOCC$_6$H$_4$COFc) and pbbm with Zn(OAc)$_2$ and subsequent crystallization should be carried out avoiding light. Thus the target polymer could be obtained. If the mixture was left under an ambient light, it rapidly yielded brown precipitate, the composition of which cannot be determined. Apparently, this is due to photolysis of the ferrocenyl-based carboxylate derivatives bearing photoactive group [8].

3.2. *Crystal structure of [Zn(o-OOCC$_6$H$_4$COFc)$_2$(pbbm)]$_n$*

The structure of [Zn(*o*-OOCC$_6$H$_4$COFc)$_2$(pbbm)]$_n$ was determined by single-crystal X-ray crystallography. The compound crystallizes in the space group *C*2/*c*. The structure consists of an infinite 1-D wave chain, in which adjacent [Zn(*o*-OOCC$_6$H$_4$COFc)$_2$] units are linked by pbbm (figure 1). *o*-Ferrocenoyl benzoate ligands are at the wave crest. Each Zn(II) ion is four-coordinate with two nitrogen atoms (N1 and N3) from two pbbm ligands and two oxygen atoms (O1 and O3) from two *o*-FcCOC$_6$H$_4$COO$^-$. The *o*-FcCOC$_6$H$_4$COO$^-$ anions are terminal monodentate

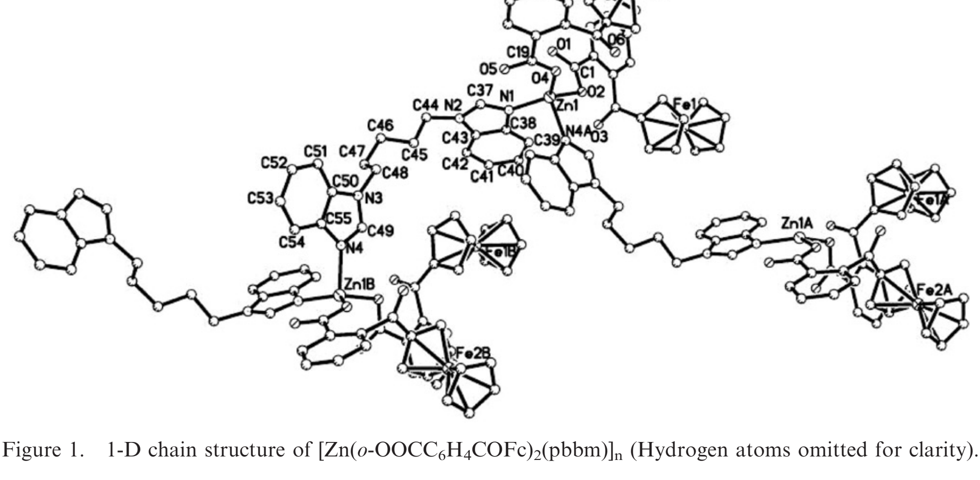


Figure 1. 1-D chain structure of [Zn(*o*-OOCC$_6$H$_4$COFc)$_2$(pbbm)]$_n$ (Hydrogen atoms omitted for clarity).

ligands to Zn(II) as in the other polymers [2i], due to the steric effects of o-$FcCOC_6H_4COO^-$.

The Zn–O bond lengths of 1.967(4) and 2.001(4) Å are slightly shorter than those in the related Zn(II) polymer, [Zn(o-$OOCC_6H_4COFc)_2$(4,4′-bipy)] (Zn–O: 2.079(4)–2.150(4) Å) [2i]. The Zn–N distances of 2.014(4) and 2.059(5) Å are close to those of the reported Zn(II) coordination polymers, for example, [Zn(o-$OOCC_6H_4COFc)_2$(4,4′-bipy)] (Zn–N: 2.142(7)–2.218(7) Å), [Zn$(OOCFc)_2$(bpt)] [2c] (Zn–N: 2.036(4)–2.077(9) Å), and [Zn$(OOCFc)_2$(bbbm)] (bbbm = 1,1′-(1,4-butanediyl)*bis*-1*H*-benzimidazole) [2h] (Zn–N: 2.028(4)–2.071(3) Å). This indicates the existence of strong interactions between Zn and ligands. The bond angles around Zn(II) range from 97.93(19)° to 126.41(19)°, aside from the smaller O2–Zn1–N4 angle of 93.51(18)°. Hence, average bond angle at Zn1 is 108.05°, slightly smaller than 109.5° for an ideal tetrahedron. Within the pbbm ligand, the benzimidazole planes are nearly planar as expected (the mean deviation from the plane is 0.0073 or 0.0184 Å). As shown in figure 1, the two pbbm ligands are mono-coordinated to Zn(II). The dihedral angle between two benzimidazole planes (N_2–C37–N1–C38–C39–C40–C41–C42–C43 and N3A–C49A–N4A–C50A–C51A–C52A–C53A–C54A–C55A) from two different pbbm ligands is 89.7°, which shows that the two benzimidazole rings are approximately perpendicular to each other. The dihedral angle between two benzimidazole planes from the same pbbm ligand is 118.4° (or 61.6°) indicating a twist of the pbbm bridge. The intra-chain distance between zinc atoms, Zn1 ··· Zn1A, is 12.614 Å, longer than that in [Zn$(OOCFc)_2$(bbp)] (Zn1 ··· Zn1: 12.180 Å) [2c] and [Zn(o-$OOCC_6H_4COFc)_2$(4,4′-bipy)] (Zn1 ··· Zn1: 11.470 Å) [2i]. Obviously, the large Zn ··· Zn separation in [Zn(o-$OOCC_6H_4COFc$)2(pbbm)]$_n$ is due to the long chain –CH_2–CH_2–CH_2–CH_2–CH_2– moiety of pbbm.

Within the ferrocenyl fragment, the average Fe–C_{ring} distance is 2.030(8) Å, in agreement with the 2.04 Å of free ferrocene. The average endocyclic C–C bond length and C–C–C angle of cyclopentadienyl rings are 1.391(12) Å and 107.6(9)°, respectively, similar to those reported in the literature [9]. The cyclopentadienyl rings are planar and nearly parallel with a dihedral angle of 3.3° at Fe1 or 0.7° at Fe_2. The intramolecular Zn1 ··· Fe1, Zn1 ··· Fe2, and Fe1 ··· Fe2 distances are 6.178, 6.893 and 8.286 Å, respectively. In the solid-state structure, the 1-D chains are packed through van der Waals interactions.

3.3. *IR spectroscopy*

Characteristic IR bands of the ferrocenyl group at 3097 and 489 cm^{-1} due to ν(C–H) and ν(Fe–Cp) vibrations, respectively [10], can be found in the polymer at 3109 and 485 cm^{-1}. Strong absorption bands at 1689 and 1563 cm^{-1} are assigned to $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ vibrations respectively, consistent with previous complexes [11]. The characteristic IR bands at 1614, 1563 and 1465 cm^{-1} indicate the presence of phenyl ring. The strong absorption band at 1652 cm^{-1} can be assigned to ν(C=O).

3.4. *Redox properties of [Zn(o-$OOCC_6H_4COFc)_2$(pbbm)]$_n$*

The molecular weight of the polymer was determined in DMF solution showing the number-average molecular weight (Mn) is 2.316×10^4, and the weight-average

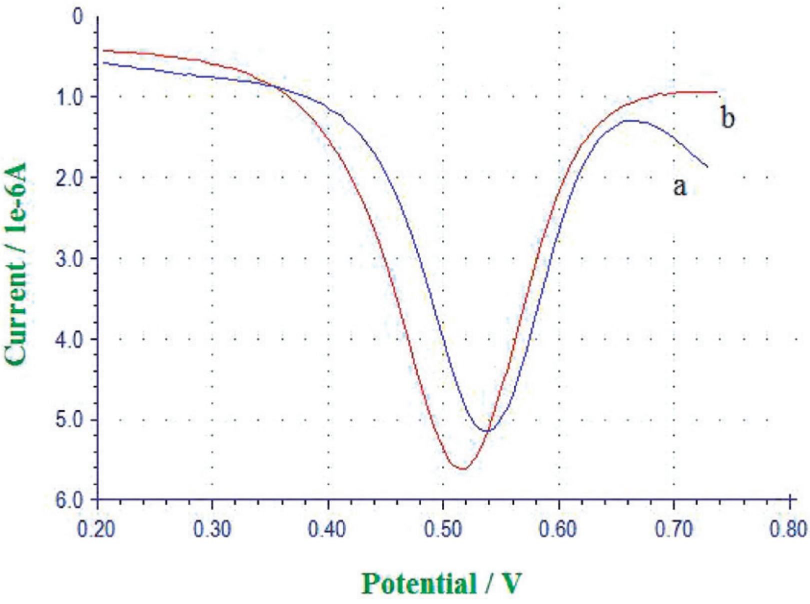


Figure 2. Differential pulse voltammogram of $[Zn(o\text{-}OOCC_6H_4COFc)_2(pbbm)]_n$ (a) and the corresponding sodium ferrocenoylbenzoate, $o\text{-}FcCOC_6OON_a$ (b) ($\sim 1.0 \times 10^{-3}$ M) in DMF containing $[Bu_4N][ClO_4]$ (0.1 M) at a scan rate of $20\,mV\,s^{-1}$.

Table 1. Crystallographic data and structure refinement for $[Zn(o\text{-}OOCC_6H_4COFc)_2(pbbm)]_n$.

Formula	$C_{55}H_{46}N_4Fe_2O_6Zn$
Formula weight	1036.03
Crystal system	Monoclinic
Crystal size (mm^3)	$0.23 \times 0.14 \times 0.11$
Space group	$C2/c$
a (Å)	28.286(10)
b (Å)	17.758(10)
c (Å)	20.480(10)
α (°)	90
β (°)	114.618(11)
γ (°)	90
V (Å^3)	9352(7)
D_c ($mg\,m^{-3}$)	1.472
Z	8
μ (mm^{-1})	1.178
Reflections collected/unique	35520/8699 [$R_{(int)} = 0.0831$]
Data/restraints/parameters	8699/0/613
Refinement method	Full-matrix least-squares on F^2
Final R indices	$R_1 = 0.0621$, $wR_2 = 0.1659$
R indices (all data)	$R_1 = 0.1238$, $wR_2 = 0.2093$
Goodness-of-fit on F_2	1.016
$\Delta\rho_{min}$ and $\Delta\rho_{max}$ (e Å^{-3})	−0.317 and 0.398

molecular weight (Mw) is 3.147×10^4. Thus, we can confirm that polymer is intact in DMF solution and shows some stability in this solvent. The results are consistent with the previous molecular weight determination of the Mn(II) and Cd(II) coordination polymers generated from *p*-ferrocenylbenzoic acid ($p\text{-}HOOCC_6H_4Fc$) [12].

Table 2. Selected bond distances (Å) and angles (°) for $[Zn(o\text{-}OOCC_6H_4COFc)_2(pbbm)]_n$.

Zn(1)–N(1)	2.014(4)	Zn(1)–O(4)	1.967(4)
Zn(1)–N(4)#1	2.059(5)	Zn(1)–O(2)	2.001(4)
O(1)–C(1)	1.246(8)	O(2)–C(1)	1.250(8)
O(3)–C(19)	1.230(8)	O(4)–C(19)	1.230(8)
O(4)–Zn(1)–O(2)	114.98(19)	N(1)–Zn(1)–O(4)	126.41(19)
N(1)–Zn(1)–O(2)	111.91(19)	O(4)–Zn(1)–N(4)#1	103.56(19)
O(2)–Zn(1)–N(4)#1	93.51(18)	N(1)–Zn(1)–N(4)#1	97.93(19)
C(1)–O(2)–Zn(1)	102.4(4)	C(19)–O(4)–Zn(1)	117.5(4)
C(37)–N(1)–C(38)	104.9(5)	C(37)–N(1)–Zn(1)	130.3(4)
O(1)–C(1)–O(2)	122.9(6)	C(38)–N(1)–Zn(1)	124.7(4)
O(1)–C(1)–C(2)	119.2(6)	(4)–C(19)–O(5)	123.9(7)
O(4)–C(19)–C(20)	118.4(7)	O(5)–C(19)–C(20)	117.7(7)
N(1)–C(37)–N(2)	113.4(5)	C(37)–N(1)–C(38)	104.9(5)
C(37)–N(1)–Zn(1)	130.3(4)	C(38)–N(1)–Zn(1)	124.7(4)
C(49)–N(4)–Zn(1)#2	127.0(4)	C(55)–N(4)–Zn(1)#2	127.3(4)

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

The solution-state differential pulse voltammetry (DPV) of the polymer $[Zn(o\text{-}OOCC_6H_4COFc)_2(pbbm)]_n$ and the ferrocenoylcarboxylate ligand (as its sodium salt $Na(o\text{-}OOCC_6H_4COFc)$) are shown in figure 2. Each exhibits a single peak with half-wave potential at 0.540 V for $\{[Zn(o\text{-}OOCC_6H_4COFc)_2(pbbm)] \cdot 2H_2O\}_n$ and 0.516 V for $Na(o\text{-}OOCC_6H_4COFc)$. The oxidation peaks correspond to the redox processes of ferrocenyl moieties. The half-wave potential of ferrocenyl in the polymer is shifted to higher potential by 0.024 V, compared with that of the free $o\text{-}FcCOC_6H_4COO^-$. It is apparent that the Zn(II) ions has an influence on the half-wave potential of the ferrocenyl moieties; similar behavior can be found in the related polymer $[Zn(o\text{-}OOCC_6H_4COFc)_2(4,4'\text{-}bipy)]$ [2i]. The difference in the electrochemical behavior of the polymer and corresponding ferocenyl ligand is due to the electron-withdrawing nature of the coordinated metal centers that make the ferrocene unit harder to oxidize [13]. At the same time, no electronic communication between the different ferrocenyl subunits was observed from the electrochemical data.

Supplementary material

Crystallographic data for the structure reported in this paper in the form of CIF file has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-631270. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44 1223 336 033; Email: deposit@ccdc.cam.ac.uk).

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References

[1] (a) D.W. Slocum, C.R. Ernst. *Adv. Organomet. Chem.*, **10**, 106 (1972); (b) A. Togni, T. Hayashi. *Ferrocenes Homogenous Catalysis, Organic Synthesis, Materials Science*, VCH publisher, New York (1995); (c) A. Togni, R.L. Haltermann (Eds). *Metallocenes*, Wiley-VCH: New York (1998); (d) W. Frosch, S. Back, H. Lang. *Organometallics*, **18**(26), 5725 (1999); (e) X.R. Meng, H.W. Hou, G. Li, B.X. Ye, T.Z. Ge, Y.T. Fan, Y. Zhu, H. Sakiyam. *J. Organomet. Chem.*, **689**, 1218 (2004); (f) T.A. Zevaco, H. Görls, E. Dinjus. *Polyhedron*, **17**(4), 613 (1998); (g) J. Yang, J.F. Ma, Y.Y. Liu, S.L. Li, G.L. Zheng. *Eur. J. Inorg. Chem.*, **11**, 2174 (2005); (h) F.A. Cotton, L.M. Daniels, C. Lin, C.A. Murillo. *J. Am. Chem. Soc.*, **121**(18), 4538 (1999); (i) H.W. Hou, G. Li, L.K. Li, Y. Zhu, X.R. Meng, Y.T. Fan. *Inorg. Chem.*, **42**, 428 (2003).

[2] (a) D. Guo, B.G. Zhang, C.Y. Duan, X. Cao, Q.J. Meng. *J. Chem. Soc., Dalton Trans.*, 282 (2003); (b) D. Guo, H. Mo, C.Y. Duan, F. Lu, Q.J. Meng. *J. Chem. Soc., Dalton Trans.*, 2593 (2002); (c) H.W. Hou, L.K. Li, G. Li, Y.T. Fan, Y. Zhu. *Inorg. Chem.*, **42**, 3501 (2003); (d) N. Prokopuk, D.F. Shriver. *Inorg. Chem.*, **36**, 5609 (1997); (e) R. Graziani, U. Casellato, G. Plazzogna. *J. Organomet. Chem.*, **187**, 381 (1980); (f) G. Li, H.W. Hou, L.K. Li, X.R. Meng, Y.T. Fan, Y. Zhu, *J. Organomet. Chem.*, **679**, 153 (2003); (i) X.R. Meng, G. Li, H.W. Hou, H.Y. Han, Y.T. Fan, Y. Zhu, C.X. Du. *Inorg. Chem.*, **42**, 4995 (2003); (j) G. Li, H.W. Hou, Z.F. Li, X.R. Meng, Y.T. Fan. *New J. Chem.*, **28**, 1595 (2004); (h) G. Li, Z.F. Li, H.W. Hou, X.R. Meng, Y.T. Fan, W.H. Chen. *J. Mol. Struct.*, **694**(1–3), 179 (2004).

[3] T.V. Baukova, L.G. Kuz'mina, N.V. Dvortsova. *Zhurnal Neorganicheskoi Khimii.*, **37**(7), 1497 (1992).

[4] X.R. Meng, B. Xiao, Y.T. Fan, H.W. Hou, G. Li. *Inorg. Chim. Acta*, **357**, 1471 (2004).

[5] A.G. Merzhanov, E.G. Klimchuk, V.K. Syundyukova, V.D. Vilchevskaya, Y.Y. Gorelikova. *Izobreteniya*, **15**, 110 (1997).

[6] X.Y. Xie, G.S. Yang, L. Cheng, F. Wang. *Huaxue Shijie*, **22**, 222 (2000).

[7] P. McArdle. *SHELX-97 User Guide;* Crystallography Center, Chemistry, Department, National University of Ireland, Galway, Ireland, P. McArdle *J. Appl. Cryst.*, **28**, 65 (1995).

[8] (a) P. Bergamini, S.D. Martino, A. Maldotti, S. Sostero. *J. Organomet. Chem.*, **365**, 341 (1989) (b) L.H. Ali, A. Cox, T.J. Kamp. *J. Chem. Soc. Dalton Trans.*, 1468 (1973).

[9] (a) A.L. Abuhijleh, C. Woods. *J. Chem. Soc., Dalton Trans.*, 1249 (1992); (b) F. Takusagawa, T.F. Koetzle. *Acta Crystallogr.*, **B35**, 2888 (1979); (c) T.H. Allen, O. Kennard. *Chem. Des. Automat. News*, **8**, 146 (1993).

[10] F.A. Cotton, L.R. Falvello, A.H. Reid, J.H. Tocher. *J. Organomet. Chem.*, **319**, 87 (1987).

[11] (a) K. Aparna, S.S. Krishnamurthy, M. Nethaji, P. Balaram. *Polyhedron*, **16**, 507 (1997); (b) F. Ribot, P. Toledano, C. Sanchez. *Inorg. Chim. Acta*, **185**, 239 (1991).

[12] H.W. Hou, L.K. Li, Y. Zhu, Y.T. Fan, Y.Q. Qiao. *Inorg. Chem.*, **43**, 4767 (2004).

[13] E.M. Barranco, O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, C. Sarroca. *J. Chem. Soc., Dalton Trans.*, 2523 (2001).