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Article

Self-Assembly of a Series of Novel Metal–Organic Compounds Containing Ferrocenecarboxylate Components

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Using FcCOONa (Fc = (η^5-C_5H_5)Fe(η^5-C_5H_4)) as starting material, we obtained an unprecedented metal–organic coordination polymer containing ferrocenecarboxylate components {[Pb_2(FcCOO)(η^2-FcCOO)(μ_2-η^2-FcCOO)(μ_3-η^2-FcCOO)(CH_3OH)]·1.5CH_3OH·H_2O}$_n$ (**1**), tetramer [Zn_4(μ_2-FcCOO)$_6$(μ_4-O)] (**2**), and coordination polymers [Pb(FcCOO)(μ_2-FcCOO)(bpe)]$_n$ (**3**) (bpe = 1,2-bis(4-pyridyl)ethene), {[Zn(FcCOO)$_2$(bpt)]·2.5H_2O}$_n$ (**4**) (bpt = *N*,*N*′-bis(3-pyridylmethyl)thiourea), and [Zn(FcCOO)(η^2-FcCOO)(bbp)]$_n$ (**5**) (bbp = 4,4′-trimethylene-dipyridine). Compounds **1** and **2** are formed by ferrocenecarboxylate units coordinating with Pb(II) or Zn(II). In polymer **1**, ferrocenecarboxylate units have four kinds of coordinate modes; just these novel coordinate modes lead to the unprecedented one-dimensional polymer where two kinds of rhomboids are arranged alternatively along the chain. Compound **2** is a tetramer, in which a distinct connectivity of the six ferrocene units is established through the four Zn atoms. Compounds **3**–**5** are obtained by organic ligands bridging Pb(II) or Zn(II), leading to a new type of metal–organic coordination polymer.

Introduction

Crystal engineering of supramolecular architectures is attractive due to their special properties, such as electrical conductivity, magnetism, host–guest chemistry, and catalysis.[1–5] Coordination polymers are one of the most important supramolecular architectures because of the formation of fascinating structures with potential in applications, for example, "bipyridyl-based" polymers with diamondoid, honeycomb, square grid, ladder, brick, octahedral, and T-shaped structure,[6–14] the polymers with macrocyclic structure,[15–17] polyoxomolybdate or vanadate cluster anions-containing polymers,[18–20] etc. There are only several examples about metal–organic coordination polymers containing ferrocene components, such as [Sm{Fc(COO)$_2$}$_{1.5}$]$_n$, [NaZn$_3${Fc(COO)$_2$}$_2$(OH)$_3$(H_2O)]$_n$ (Fc = (η^5-C_5H_4)Fe(η^5-C_5H_4)), and {[M(4-dptf)](PF$_6$)}$_n$ (M = Cu, Ag; 4-dptf = 1,1′-(4-dipyridinethio)ferrocene).[21–23]

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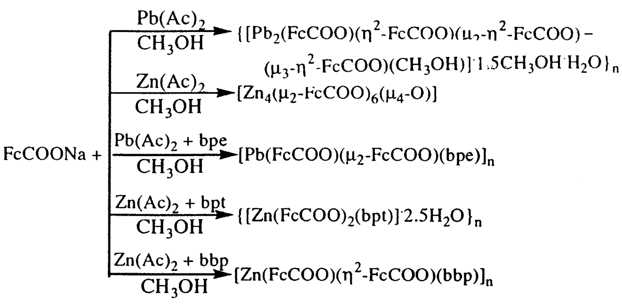
Up to now, a wide variety of metal complexes containing ferrocene derivatives have been described,[24−29] and ferrocenecarboxylate-containing ligands have also been used in the syntheses strategy, but the reported several ferrocenecarboxylate-containing compounds are discrete oligomers, such as dimeric tetrabridged complexes $[M_2(\mu\text{-OOCFc})_4]$ (M = Cu, Mo)[28,30] (Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$), trinuclear cluster $\{n\text{-BuSnCl(OOCFc)}\}_3(O)(OH)$,[31] tin−oxygen cluster $[\{BuSn(O)OC(O)Fc\}_6]$,[32] mononuclear ferrocenecarboxylate Cu(II) complexes *trans*-$[Cu(OOCFc)_2(py)_2]$ and *trans*-$[Cu(OOCFc)_2(imid)_2]$ (imid = imidazole),[33] etc.; these compounds only are mono- or polynuclear ferrocenecarboxylate complexes, in which ferrocenecarboxylate anions act as simple terminal monodentate or bidentate ligands. Coordination polymers containing ferrocenecarboxylate anions are rare. To the authors' knowledge, only a few ferrocenecarboxylate polymers have been reported, such as one-dimensional linear polymers $FcCOOSn(CH{=}CH_2)_3$[34] and $Na_2Mo_6Cl_8(OOCFc)_6{\cdot}CH_3OH$.[27]

Our strategy is to attach the ferrocenecarboxylate components to coordination polymers and, then, produce a new kind of compounds, metal−organic coordination polymers containing ferrocenecarboxylate components. It is known that until now the development of metal−organic polymers still offer a considerable synthetic challenge. On the basis of synthetic methods of coordination polymers, we easily prepare metal-organic coordination polymers. Herein, using FcCOONa (Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$) as starting material to react with $Pb(Ac)_2$ (or $Zn(Ac)_2$) and organic ligands, we obtain unprecedented metal−organic polymer $\{[Pb_2(FcCOO)(\eta^2\text{-FcCOO})(\mu_2\text{-}\eta^2\text{-FcCOO})(\mu_3\text{-}\eta^2\text{-FcCOO})(CH_3OH)]{\cdot}1.5CH_3OH{\cdot}H_2O\}_n$ (**1**), tetramer $[Zn_4(\mu_2\text{-FcCOO})_6(\mu_4\text{-O})]$ (**2**), and polymers $[Pb(FcCOO)(\mu_2\text{-FcCOO})(bpe)]_n$ (**3**) (bpe = 1,2-bis(4-pyridyl)ethene), $\{[Zn(FcCOO)_2(bpt){\cdot}2.5H_2O]_n$ (**4**) (bpt = *N*,*N*′-bis(3-pyridylmethyl)thiourea), and $[Zn(FcCOO)(\eta^2\text{-FcCOO})(bbp)]_n$ (**5**) (bbp = 4,4′-trimethylene-dipyridine).



1

2

3

4

5

Experimental Section

General Considerations. The chemicals and solvents used in synthesis of complexes were of A.R. grade and used without further purification. Sodium ferrocenecarboxylate (FcCOONa) was prepared as described previously.[35]

IR spectra were recorded on a Fourier Nicolet FT-170SX spectrophotometer with pressed KBr pellets in the 400−4000 cm^{-1} region. Carbon, hydrogen, and nitrogen analyses were performed by a Carlo-Erba 1106 elemental analyzer. TGA-DTA measurements were performed by heating the sample from 20 to 900 °C at a rate of 10 °C min^{-1} in air on a Perkin-Elmer DTA-7 differential thermal analyzer.

Synthesis of $\{[Pb_2(FcCOO)(\eta^2\text{-FcCOO})(\mu_2\text{-}\eta^2\text{-FcCOO})(\mu_3\text{-}\eta^2\text{-FcCOO})(CH_3OH)]{\cdot}1.5CH_3OH{\cdot}H_2O\}_n$ (1). FcCOONa (5.04 mg, 0.02 mmol) in CH_3OH (5 mL) was added dropwise to a CH_3OH solution (4 mL) of $Pb(Ac)_2{\cdot}3H_2O$ (3.80 mg, 0.01 mmol). The resulting pale yellow solution was allowed to stand at room temperature in the dark. Good quality red crystals were obtained after several days. Crystals of **1** are unstable in the air. Yield: 74%. Anal. Calcd for $C_{93}H_{94}Fe_8O_{23}Pb_4$: C, 39.41; H, 3.32%. Found: C, 40.47; H, 3.15%. IR (cm^{-1}, KBr): 3423 (m), 1517 (s), 1468 (s), 1386 (s), 1356 (s), 1344 (m), 811(m), 792 (m), 509 (m).

Synthesis of $[Zn_4(\mu_2\text{-FcCOO})_6(\mu_4\text{-O})]$ (2). The 6 mL CH_3OH solution of FcCOONa (5.04 mg, 0.02 mmol) was dropped slowly into the 8 mL CH_3OH solution of $Zn(Ac)_2{\cdot}2H_2O$ (2.19 mg, 0.01 mmol); the mixture was stirred and then put in the dark. Four days later, the fine red X-ray quality single crystals were obtained. Crystals of **2** are unstable in the air. Yield: 85%. Anal. Calcd for $C_{66}H_{54}Fe_6O_{13}Zn_4$: C, 47.99; H, 3.30%. Found: C, 46.47; H, 3.75%. IR (cm^{-1}, KBr): 3431 (m), 1561 (s), 1480 (s), 1392 (s), 1360 (s), 1194 (m), 821 (m), 516 (m).

Synthesis of $[Pb(FcCOO)(\mu_2\text{-FcCOO})(bpe)]_n$ (3). The ligand bpe (3.64 mg, 0.02 mmol) (bpe = 1,2-bis(4-pyridyl)ethene) in 5 mL of CH_3OH was added dropwise to a solution of FcCOONa (5.04 mg, 0.02 mmol) and $Pb(Ac)_2{\cdot}3H_2O$ (3.80 mg, 0.01 mmol) in 8 mL of CH_3OH. Red single crystals were obtained after the reaction mixture was put in the dark for one week. The compound is unstable in the air. Yield: 69%. Anal. Calcd for $C_{34}H_{28}Fe_2N_2O_4Pb$: C, 48.19; H, 3.33; N, 3.31%. Found: C, 48.47; H, 3.75; N, 3.03%. IR (cm^{-1}, KBr): 3441 (m), 1647 (s), 1602 (s), 1559 (s), 1377 (s), 1289 (m), 1002 (m), 828 (m), 551 (m).

Synthesis of $\{[Zn(FcCOO)_2(bpt)]{\cdot}2.5H_2O\}_n$ (4). The 6 mL CH_3OH solution of bpt (5.16 mg, 0.02 mmol) (bpt = *N*,*N*′-bis(3-pyridylmethyl)thiourea) was added dropwise to an 8 mL CH_3OH solution containing 5.04 mg (0.02 mmol) of FcCOONa and 2.19 mg (0.01 mmol) of $Zn(Ac)_2{\cdot}2H_2O$; the mixture solution was stirred at room temperature, and then put in the dark, and red crystals suitable for X-ray determination were yielded several days later. Yield: 72%. Anal. Calcd for $C_{35}H_{38}Fe_2N_4O_{6.5}SZn$: C, 50.73; H, 4.59; N, 6.76%. Found: C, 50.47; H, 4.75; N, 6.39%. IR (cm^{-1}, KBr): 3285 (m), 1554(s), 1478 (s), 1386 (s), 1341 (s), 1191 (m), 1105 (m), 797 (m), 704 (m), 512 (m).

Synthesis of $[Zn(FcCOO)(\eta^2\text{-FcCOO})(bbp)]_n$ (5). Compound **5** was prepared in a manner analogous to that used to prepare **4** except that bbp (3.96 mg, 0.02 mmol) (bbp = 4,4′-trimethylene-dipyridine) was used instead of bpt. The reaction system was also

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Table 1. Crystallographic Data for Polymers **1**, **2**, **3**, **4**, and **5**

	1	**2**	**3**	**4**	**5**
empirical formula	$C_{93}H_{94}Fe_8O_{23}Pb_4$	$C_{66}H_{54}Fe_6O_{13}Zn_4$	$C_{34}H_{28}N_2Fe_2O_4Pb$	$C_{35}H_{38}N_4Fe_2O_{6.5}SZn$	$C_{35}H_{32}N_2Fe_2O_4Zn$
fw	2855.24	1651.67	847.47	827.82	721.70
cryst syst	triclinic	triclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1c$
unit cell dimensions					
a (Å)	14.031(3)	16.094(3)	10.547(2)	12.905(3)	10.638(2)
b (Å)	14.609(3)	17.895(4)	11.101(2)	13.619(3)	12.764(3)
c (Å)	12.035(2)	11.402(2)	13.882(3)	11.845(2)	22.652(5)
α (deg)	93.92(3)	106.70(3)	109.90(3)	90.09(3)	90
β (deg)	99.74(3)	102.01(3)	106.04(3)	109.15(3)	90.45(3)
γ (deg)	72.52(3)	81.24(3)	93.44(3)	71.34(3)	90
Z	1	2	2	2	4
T (K)	291(2)	291(2)	291(2)	293(2)	291(2)
ρ (Mg m^{-3})	2.045	1.792	1.945	1.485	1.559
F (000)	1372	1660	824	852	1480
cryst size (mm^3)	0.30 × 0.20 × 0.20	0.25 × 0.20 × 0.20	0.25 × 0.20 × 0.20	0.25 × 0.20 × 0.20	0.25 × 0.20 × 0.20
V (Å^3)	2318.7(8)	3061.5(11)	1447.1(5)	1850.8(6)	3075.6(11)
reflns collected	8515	7086	5462	5512	8975
reflns obsd	8515	7086	5462	5512	5398
no. variables	574	839	389	456	406
GOFt indicator	1.091	1.099	1.092	1.015	1.092
extinction coeff	0.0020(2)	0.00000(14)	0.00624(14)	0.0015(4)	0.00192(17)
final R indices $I > 2.00\sigma(I)$	$R = 0.0543$	$R = 0.0744$	$R = 0.0362$	$R = 0.0674$	$R = 0.0542$
	$R_w = 0.1315$	$R_w = 0.1924$	$R_w = 0.0704$	$R_w = 0.1439$	$R_w = 0.1114$
R (all data)	$R = 0.0743$	$R = 0.0935$	$R = 0.0425$	$R = 0.1345$	$R = 0.0806$
	$R_w = 0.1412$	$R_w = 0.2027$	$R_w = 0.0726$	$R_w = 0.1666$	$R_w = 0.1202$
$\Delta\rho_{min}$ and $\Delta\rho_{max}$ (e·Å^{-3})	−2.602 and 2.057	−0.743 and 1.735	−1.444 and 0.798	−0.496 and 0.603	−0.394 and 0.408

put in the dark for 3 days, from which red X-ray quality single crystals were obtained. Yield: 80%. Anal. Calcd for $C_{35}H_{32}Fe_2N_2O_4Zn$: C, 58.25; H, 4.47; N, 3.88%. Found: C, 58.47; H, 4.75; N, 3.54%. IR (cm^{-1}, KBr): 3440 (m), 1618 (s), 1586 (s), 1472 (s), 1384 (s), 1354 (m), 1336 (s), 1024 (m), 812 (m), 795 (m), 512 (m).

X-ray Crystallography. All the data were collected on a Rigaku RAXIS-IV imaging plate area detector diffractometer using graphite monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å). A prismatic single crystal was mounted on a glass fiber. The data were collected at a temperature of 18 ± 1 °C and corrected for Lorenz-polarization effects. A correction for secondary extinction was applied. The structures were solved by direct methods and expanded using 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 using the *SHELXL-97* program. Crystallographic data for compounds **1**, **2**, **3**, **4**, and **5** are given in Table 1. Selected bond lengths and bond angles are given in Table 2.

Results and Discussion

Crystal Structure of {[Pb$_2$(FcCOO)(η^2-FcCOO)(μ_2-η^2-FcCOO)(μ_3-η^2-FcCOO)(CH$_3$OH)] ·1.5CH$_3$OH·H$_2$O}$_n$ (1). X-ray diffraction analysis reveals that **1** is a one-dimensional chain structural polymer (Figure 1), which contains two kinds of Pb ions and four kinds of FcCOO$^-$ units. Pb ions are bridged by oxygen atoms from FcCOO$^-$ units forming a ···Pb1Pb1Pb2Pb2Pb1Pb1··· chain; Pb1···Pb1, Pb1···Pb2, and Pb2···Pb2 distances are 4.251, 4.409, and 4.417 Å, respectively. It is noteworthy that the four kinds of FcCOO$^-$ units are monodentate (FcCOO$^-$), bidentate (η^2-FcCOO$^-$), tridentate (μ_2-η^2-FcCOO$^-$), and tetradentate (μ_3-η^2-FcCOO$^-$)-ligands (Chart 1), respectively, and this case is very rare.

In the structure unit (Figure 2), each Pb1 atom binds to two O atoms from a chelating η^2-FcCOO$^-$ unit, three O atoms from two μ_2-η^2-FcCOO$^-$ units, and one O atom from a μ_3-η^2-FcCOO$^-$ unit. The six coordinate oxygen atoms around the Pb1 form a boat conformation; each Pb1 atom lies in the inner of the boat, where O1, O2, O3, O4 are coplanar and constitute the bottom of the boat, O3 and O4 come from one η^2-FcCOO$^-$ unit, and O1 and O2 are from one μ_2-η^2-FcCOO$^-$ unit. The distance from Pb1 to the planar O1−O2−O3−O4 is 1.2521 Å. Each Pb2 atom coordinates to one O(O8) atom from one FcCOO$^-$ unit, three O atoms (O5, O6, O5#1) from two μ_3-η^2-FcCOO$^-$ units, and one

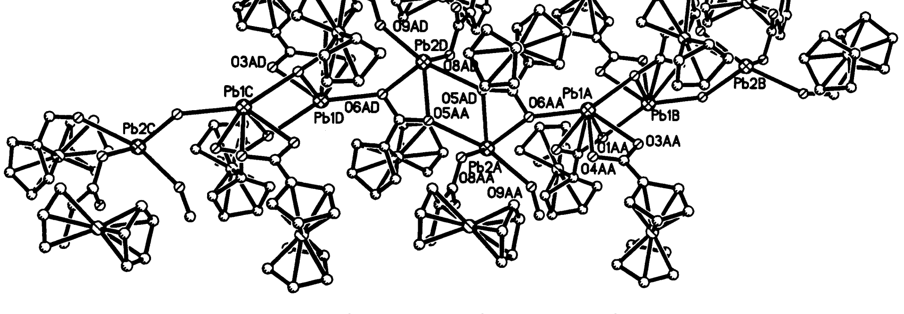

Figure 1. One-dimensional chain structure of {[Pb$_2$(FcCOO)(η^2-FcCOO)(μ_2-η^2-FcCOO)(μ_3-η^2-FcCOO)(CH$_3$OH)]·1.5CH$_3$OH·H$_2$O}$_n$.

Table 2. Selected Bonds Distances (Å) and Angles (deg) for **1**, **2**, **3**, **4**, and **5**[a]

		Polymer **1**			
Pb(1)−O(2)	2.430(9)	Pb(1)−O(1)	2.464(8)	Pb(1)−O(4)	2.516(9)
Pb(1)−O(3)	2.530(8)	Pb(1)−O(6)	2.659(7)	Pb(1)−O(1)#1	2.726(8)
Pb(2)−O(6)	2.445(8)	Pb(2)−O(5)#2	2.592(9)	Pb(2)−O(8)	2.371(7)
Pb(2)−O(9)	2.651(9)	O(1)−Pb(1)#1	2.726(8)	Pb(2)−O(5)	2.647(8)
O(5)−Pb(2)#2	2.591(8)	O(2)−Pb(1)−O(4)	83.0(3)	O(1)−Pb(1)−O(4)	101.7(3)
O(2)−Pb(1)−O(1)	52.7(2)	O(1)−Pb(1)−O(3)	74.8(3)	O(4)−Pb(1)−O(3)	51.7(3)
O(2)−Pb(1)−O(3)	100.5(3)	O(1)−Pb(1)−O(6)	123.8(3)	O(4)−Pb(1)−O(6)	72.2(2)
O(2)−Pb(1)−O(6)	71.3(2)	O(2)−Pb(1)−O(1)#1	119.7(2)	O(1)−Pb(1)−O(1)#1	70.1(3)
O(3)−Pb(1)−O(6)	123.9(3)	O(3)−Pb(1)−O(1)#1	79.4(3)	O(6)−Pb(1)−O(1)#1	153.9(2)
O(4)−Pb(1)−O(1)#1	130.1(3)	O(8)−Pb(2)−O(5)#2	75.4(3)	O(6)−Pb(2)−O(5)#2	51.2(2)
O(8)−Pb(2)−O(6)	86.1(3)	O(6)−Pb(2)−O(5)	116.3(2)	O(5)#2−Pb(2)−O(5)	65.0(3)
O(8)−Pb(2)−O(5)	76.3(2)	O(6)−Pb(2)−O(9)	67.2(3)	O(5)#2−Pb(2)−O(9)	113.5(3)
O(8)−Pb(2)−O(9)	78.3(3)	O(5)−Pb(2)−O(9)	154.0(3)	Pb(1)−O(1)−Pb(1)#1	109.9(3)
Pb(2)#2−O(5)−Pb(2)	115.0(3)	Pb(1)−O(1)−Pb(1)#1	109.9(3)	Pb(2)−O(6)−Pb(1)	119.5(3)
		Polymer **2**			
Zn(1)−O(16)	1.837(9)	Zn(1)−O(2)	1.997(8)	Zn(1)−O(4)	2.013(10)
Zn(1)−O(10)	2.048(10)	Zn(2)−O(7)	1.966(9)	Zn(2)−O(16)	1.947(8)
Zn(2)−O(5)	1.965(8)	Zn(2)−O(9)	1.977(9)	Zn(3)−Zn(4)	3.139(2)
Zn(2)−Zn(4)	3.123(2)	Zn(2)−Zn(3)	3.143(2)	Zn(3)−O(8)	1.954(9)
Zn(3)−O(1)	1.971(10)	Zn(3)−O(12)	1.971(9)	Zn(3)−O(16)	1.993(8)
Zn(4)−O(11)	1.947(9)	Zn(4)−O(3)	1.970(9)	Zn(4)−O(6)	1.962(9)
Zn(4)−O(16)	2.001(8)				
O(16)−Zn(1)−O(2)	109.8(3)	O(16)−Zn(1)−O(4)	109.0(4)	O(2)−Zn(1)−O(4)	112.2(4)
O(16)−Zn(1)−O(10)	106.4(3)	O(2)−Zn(1)−O(10)	109.8(4)	O(4)−Zn(1)−O(10)	109.4(4)
O(16)−Zn(2)−O(5)	108.1(4)	O(16)−Zn(2)−O(7)	109.8(4)	O(5)−Zn(2)−O(7)	112.8(4)
O(16)−Zn(2)−O(9)	102.3(4)	O(5)−Zn(2)−O(9)	111.2(4)	O(9)−Zn(2)−O(7)	112.1(3)
O(16)−Zn(2)−Zn(4)	38.3(2)	O(5)−Zn(2)−Zn(4)	69.9(3)	O(7)−Zn(2)−Zn(4)	129.0(3)
O(9)−Zn(2)−Zn(4)	113.7(3)	O(16)−Zn(2)−Zn(3)	37.6(2)	O(5)−Zn(2)−Zn(3)	112.6(2)
O(7)−Zn(2)−Zn(3)	74.2(2)	O(9)−Zn(2)−Zn(3)	128.1(3)	Zn(4)−Zn(2)−Zn(3)	60.11(5)
O(8)−Zn(3)−O(1)	110.1(4)	O(8)−Zn(3)−O(12)	114.8(4)	O(1)−Zn(3)−O(12)	111.5(4)
O(8)−Zn(3)−O(16)	107.1(4)	O(1)−Zn(3)−O(16)	104.3(4)	O(12)−Zn(3)−O(16)	108.4(4)
O(8)−Zn(3)−Zn(4)	109.7(3)	O(1)−Zn(3)−Zn(4)	132.3(3)	O(12)−Zn(3)−Zn(4)	73.2(3)
O(16)−Zn(3)−Zn(4)	38.3(2)	O(8)−Zn(3)−Zn(2)	71.0(3)	O(1)−Zn(3)−Zn(2)	111.8(3)
O(12)−Zn(3)−Zn(2)	130.1(3)	O(16)−Zn(3)−Zn(2)	36.6(2)	Zn(4)−Zn(3)−Zn(2)	59.63(5)
O(11)−Zn(4)−O(6)	111.6(4)	O(11)−Zn(4)−O(3)	113.7(4)	O(3)−Zn(4)−O(6)	109.5(4)
O(11)−Zn(4)−O(16)	106.2(4)	O(6)−Zn(4)−O(16)	111.7(4)	O(3)−Zn(4)−O(16)	103.8(4)
O(11)−Zn(4)−Zn(2)	109.4(3)	O(6)−Zn(4)−Zn(2)	76.8(3)	O(3)−Zn(4)−Zn(2)	129.2(3)
O(16)−Zn(4)−Zn(2)	37.1(2)	O(11)−Zn(4)−Zn(3)	68.6(3)	O(6)−Zn(4)−Zn(3)	132.3(3)
O(3)−Zn(4)−Zn(3)	113.3(3)	O(16)−Zn(4)−Zn(3)	38.1(2)	Zn(2)−Zn(4)−Zn(3)	60.26(5)
		Polymer **3**			
Pb(1)−O(3)	2.334(3)	Pb(1)−O(1)	2.364(3)	Pb(1)−O(4)	2.939(3)
Pb(1)−N(2)	2.702(4)	Pb(1)−N(1)	2.580(3)		
O(3)−Pb(1)−O(1)	83.54(11)	O(3)−Pb(1)−N(1)	79.86(11)	O(1)−Pb(1)−N(1)	80.70(11)
O(3)−Pb(1)−N(2)	85.95(12)	O(1)−Pb(1)−N(2)	80.92(12)	N(1)−Pb(1)−N(2)	157.88(12)
		Polymer **4**			
Zn(1)−O(1)	1.946(4)	Zn(1)−O(3)	1.977(4)	Zn(1)−N(1)	2.036(4)
Zn(1)−N(4)	2.077(4)				
O(1)−Zn(1)−O(3)	110.47(15)	O(1)−Zn(1)−N(1)	132.75(18)	O(3)−Zn(1)−N(1)	104.26(16)
O(1)−Zn(1)−N(4)	108.22(16)	O(3)−Zn(1)−N(4)	96.50(15)	N(1)−Zn(1)−N(4)	98.37(15)
		Polymer **5**			
Zn(1)−O(1)	1.989(2)	Zn(1)−O(3)	2.027(2)	Zn(1)−O(4)	2.387(2)
Zn(1)−N(1)	2.103(2)	Zn(1)−N(2)	2.108(2)		
O(1)−Zn(1)−O(3)	145.33(8)	O(1)−Zn(1)−N(1)	102.78(9)	O(3)−Zn(1)−N(1)	102.74(9)
O(1)−Zn(1)−N(2)	102.61(9)	O(3)−Zn(1)−N(2)	97.05(9)	N(1)−Zn(1)−N(2)	97.19(9)
O(1)−Zn(1)−O(4)	97.05(9)	O(3)−Zn(1)−O(4)	59.35(8)	N(1)−Zn(1)−O(4)	91.27(8)
N(2)−Zn(1)−O(4)	156.24(9)				

[a] Symmetry transformations used to generate equivalent atoms. For **1**: #1 $-x, -y+1, -z$; #2 $-x+1, -y+1, -z$; #3 $-x+1, -y+1, -z+1$. For **2** and **3**: #1 $x, y-1, z-1$; #2 $x, y+1, z+1$. For **4**: #1 $x, y+1, z$; #2 $x, y-1, z$. For **5**: #1 $-x, y-{}^{1}/_{2}, -z+{}^{1}/_{2}$; #2 $-x, y+{}^{1}/_{2}, -z+{}^{1}/_{2}$.

O(O9) atom from one CH_3OH. Pb2, O5, O8, and O9 are nearly coplanar (the mean deviation from plane is 0.086 Å); each Pb2 atom is in a trigonal bipyramid geometry, but the two apexes of the pyramid are at the same side of the bottom planar Pb2−O5−O8−O9. This can be comparable to the known lead(II) carboxylate cluster $[Pb\{(CO)_9Co_3(CCO_2)\}_2]_n$,[36] in which the connection modes between the Pb and the carboxylate O atoms are the same as the above μ_2-η^2-$FcCOO^-$ coordinate mode. Interestingly, along the ···Pb1Pb1Pb2Pb2Pb1Pb1··· chain, there are two kinds of

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(36) Lei, X. J.; Shang, M. Y.; Patil, A.; Wolf, E. E.; Fehlner, T. P. *Inorg. Chem.* **1996**, *35*, 3217.

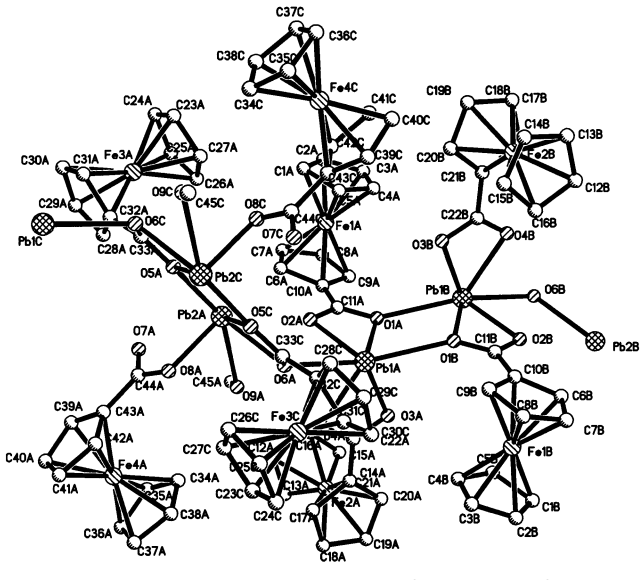
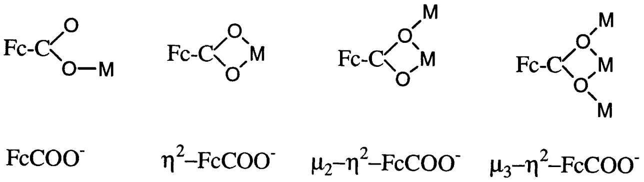


Figure 2. Structural unit of $\{[Pb_2(FcCOO)(\eta^2\text{-}FcCOO)(\mu_2\text{-}\eta^2\text{-}FcCOO)(\mu_3\text{-}\eta^2\text{-}FcCOO)(CH_3OH)]\cdot 1.5CH_3OH\cdot H_2O\}_n$.

Chart 1



rhomboid arrangements, alternatively. One is formed by two Pb1 atoms and two O atoms from two μ_2-η^2-FcCOO$^-$ units, and the other is built by two Pb2 atoms and two O atoms from two μ_3-η^2-FcCOO$^-$ units. The dimensions of the two rhomboids are 2.464 × 2.725 Å^2 and 2.591 × 2.647 Å^2, respectively, and the dihedral angle between the two rhomboids is 118.0°.

Compared with the reported ferrocenecarboxylate-containing polymers, polymer **1** shows special novelty. [FcCOOSn(CH=CH$_2$)$_3$] crystallizes as a one-dimensional polymer along the needle axis with the carboxylate groups (μ_2-FcCOO) acting to bridge the Sn units.[34] In $Na_2Mo_6Cl_8(OOCFc)_6\cdot CH_3OH$, the Na$^+$ ions link neighboring clusters through three kinds of FcCOO units (FcCOO$^-$, μ_2-FcCOO$^-$, μ_3-FcCOO$^-$), creating a one-dimensional chain containing the $[Mo_6Cl_8]^{4+}$ core.[27] Polymer **1** is formed by four kinds of FcCOO$^-$ units, FcCOO$^-$, η^2-FcCOO$^-$, μ_2-η^2-FcCOO$^-$, and μ_3-η^2-FcCOO$^-$, which bridge two kinds of Pb ions.

Crystal Structure of [Zn$_4$(μ_2-FcCOO)$_6$(μ_4-O)] (2). Compound **2** is a discrete tetramer (Figure 3). The four Zn atoms form a slightly distorted tetrahedral structure, and the O16 atom as a μ_4-O^{2-} anion occupies the center of the tetrahedral structure and bridges to the four Zn atoms; the bridging mode is similar to that of the known tetrazinc carbamato complexes $(Zn_4O)(O_2CR)_6$ (R = diethylamino, piperidino, or pyrrolidino),[37] which have the same tetrahedral Zn_4O^{6+} core. In **2**, six edges of the Zn$_4$ tetrahedron are occupied by six μ_2-FcCOO$^-$ units, in which each μ_2-FcCOO$^-$ unit links to two Zn atoms. Six Zn−O16−Zn bond angles are from 103.6° to 122.7°, and four O16−Zn bond lengths are 1.837, 1.947, 1.993, and 2.001 Å, respectively. Each Zn atom exhibits a tetrahedral coordination geometry: four coordination O atoms are from three μ_2-FcCOO$^-$ units and the μ_4-O^{2-} anion, respectively. The Zn···Zn distances are about 3.1 Å, which are a little shorter than the Zn···Zn distances in (Zn$_4$O)(O$_2$-

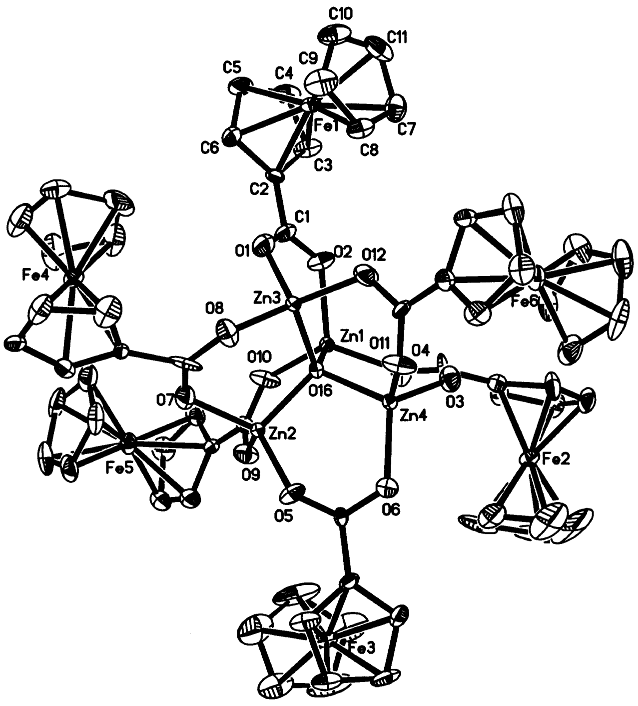


Figure 3. Crystal structure of [Zn$_4$(μ_2-FcCOO)$_6$(μ_4-O)].

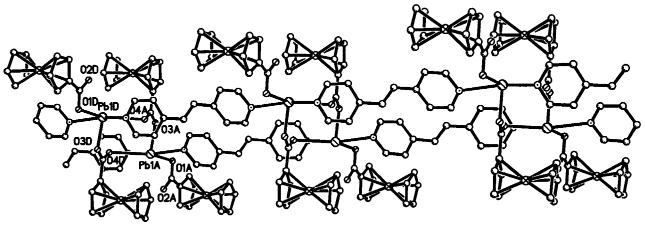


Figure 4. One-dimensional ladderlike structure of [Pb(FcCOO)(μ_2-FcCOO)(bpe)]$_n$.

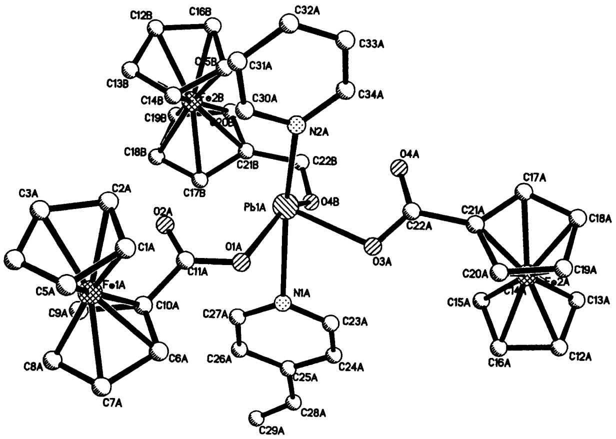


Figure 5. ORTEP diagram showing the structure unit of [Pb(FcCOO)(μ_2-FcCOO)(bpe)]$_n$.

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(37) McCowan, C. S.; Groy, T. L.; Caudle, M. T. *Inorg. Chem.* **2002**, *41*, 1120.

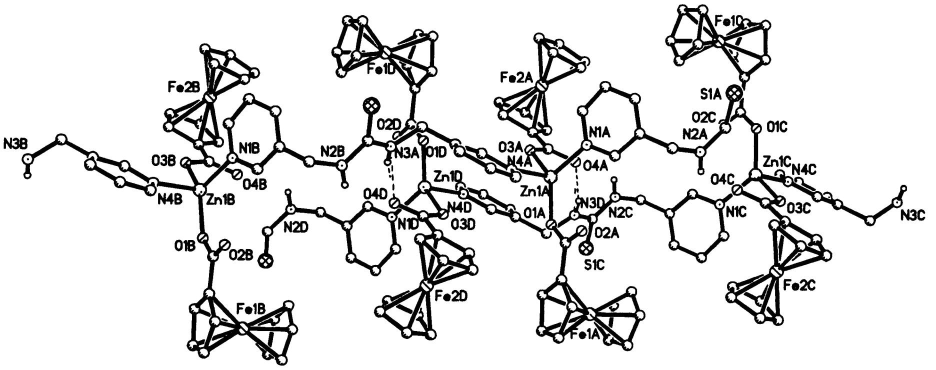

Figure 6. One-dimensional ladderlike structure of $\{[Zn(FcCOO)_2(bpt)]{\cdot}2.5H_2O\}_n$.

CR)$_6$, where Zn···Zn distances are 3.15 and 3.20 Å, respectively, in line with typical complexes having the Zn_4O^{6+} core.[38]

Six Fe atoms form a compression octahedral structure, Fe1 and Fe3 atoms occupy axial positions, and the other four Fe atoms are at equatorial positions. Polymer **2** is comparable to a known tin−oxygen ferrocenecarboxylate cluster, $[\{BuSn(O)OC(O)Fc\}_6]$,[32] whose structure shows a giant wheel arrangement with a drumlike stannoxane central core serving as the structural support for the hexaferrocene assemble. In another similar trinuclear ferrocenecarboxylate-containing complex, $\{n\text{-}BuSnCl(OOCFc)\}_3(O)(OH)$,[31] the three $FcCOO^-$ units through the μ_2-$FcCOO^-$ mode bridge the three Sn atoms, while in our case there is a distinct connectivity of the six ferrocene units established through the four Zn atoms. The distances between adjacent Fe atoms are about 7.2 Å, and two diagonal Fe atoms have the distance of about 12.4 Å. The shortest Fe−C bond lengths is 1.95(3) Å, and the longest Fe−C bond length is 2.06(2) Å. In each ferrocenyl moiety, the cyclopentadienyl rings are planar and nearly parallel.

Crystal Structure of $[Pb(FcCOO)(\mu_2\text{-}FcCOO)(bpe)]_n$ (3). Polymer **3** shows a one-dimensional ladderlike structure (Figure 4). In the structure unit, the $FcCOO^-$ units coordinate with Pb atoms by two modes, one is that one $FcCOO^-$ unit as a monodentate ligand ($FcCOO^-$) binds to one Pb atom, while the other is that the other $FcCOO^-$ unit as bridging bidentate ligand μ_2-$FcCOO^-$ binds to two Pb atoms. Each Pb atom is in a distorted tetragonal prism coordination environment and coordinates with two N atoms from different bpe units, two O atoms from two μ_2-$FcCOO^-$ units, and one O atom of one $FcCOO^-$ unit (Figure 5). $Pb-N_{(bpe)}$ bond lengths are 2.580 and 2.702 Å, respectively, which are similar to those of the known polymer $[Pb(NCS)(bpe)]_n$[39] (its $Pb-N_{(bpe)}$ bond lengths are 2.570 and 2.713 Å, respectively), and Pb−O bond lengths are in the range 2.334−2.364 Å. The angles of N1−Pb1−N2 and O1−Pb1−O3 are 157.88° and 83.54°, respectively. The bpe units connect all Pb atoms to form two infinite −Pb−bpe−Pb−bpe− chains, the two chains are parallel to each other, and the Pb···Pb distance in each chain is 14.526 Å. Also, the two chains are bridged by $Pb(\mu_2\text{-}FcCOO)_2Pb$ leading to an infinite ladderlike chain polymer; the adjacent Pb···Pb distance of the two chains is 4.654 Å.

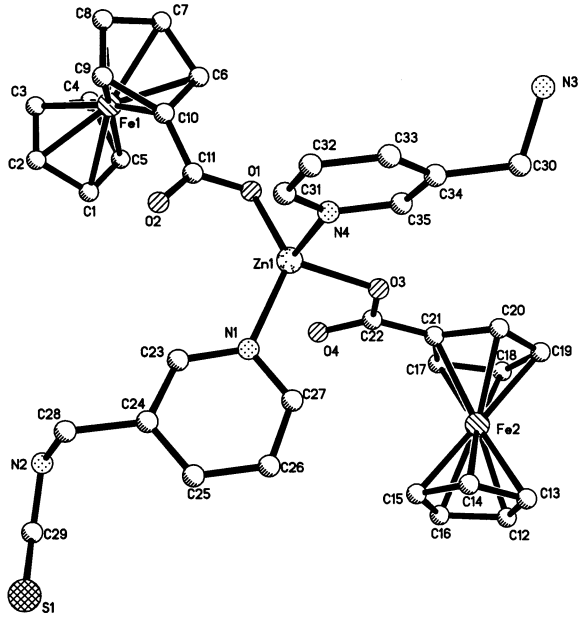

Figure 7. ORTEP diagram showing the structure unit of $\{[Zn(FcCOO)_2(bpt)]{\cdot}2.5H_2O\}_n$.

Of the reported ferrocene coordination polymers such as $\{[M(4\text{-dptf})](PF_6)\}_n$ and $[M(hfac)_2(4\text{-dptf})]_n$ (M = Cu, Ag; 4-dptf = 1,1′-(4-dipyridinethio)ferrocene), all of them exhibit a one-dimensional chain structure,[21] ferrocene units are in the main chain, and these linear chains consist of ferrocene components. The linear chain of polymer **3** is composed of Pb and bpe; ferrocene units are not in the main chain. Thus polymer **3** can be defined as a coordination polymer with ferrocene units in the side chain.

Crystal Structure of $\{[Zn(FcCOO)_2(bpt)]{\cdot}2.5H_2O\}_n$ (4). Compound **4** exhibits a one-dimensional ladderlike structure, too (Figure 6), but the structure is not the same as that of polymer **3**, in which the $FcCOO^-$ units as monodentate ($FcCOO^-$) and bidentate (μ_2-$FcCOO^-$) modes coordinate with metal atoms. In **4**, the $FcCOO^-$ units just exist as monodentate ligands coordinating with the Zn atoms. That may be due to the difference of the organic ligands. The center Zn atoms exhibit tetrahedral geometry and coordinate

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(38) Clegg, W.; Harbron, D. R.; Human, C. D.; Hunt, P. A.; Little, I. R.; Straughan, B. P. *Inorg. Chim. Acta* **1991**, *186*, 51.

(39) Niu, Y. Y.; Hou, H. W.; Zhang, Q. F.; Xin, X. Q.; Fun, H. K.; Chantrapromma, S.; Razak, A. *Acta Crystallogr.* **2001**, *57*, 526.

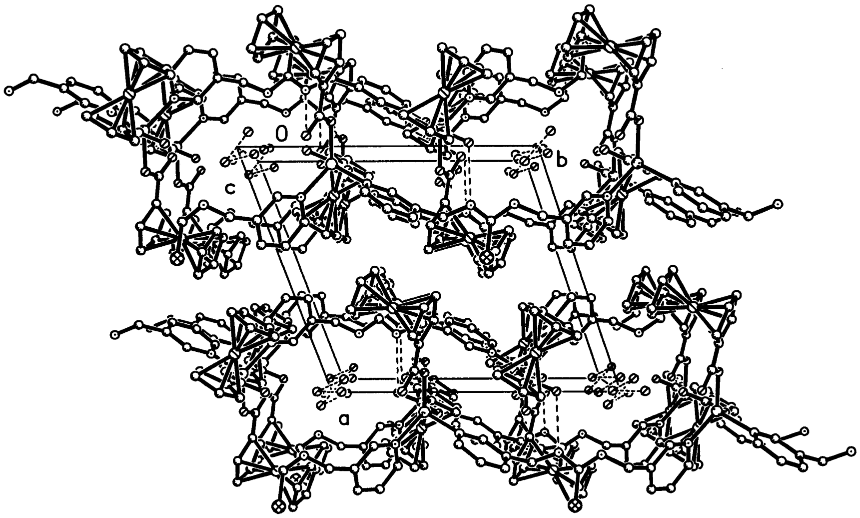

Figure 8. Solid state structure of $\{[Zn(FcCOO)_2(bpt)]\cdot 2.5H_2O\}_n$ containing large pores with the dimensions of 10.058 × 7.821 Å^2.

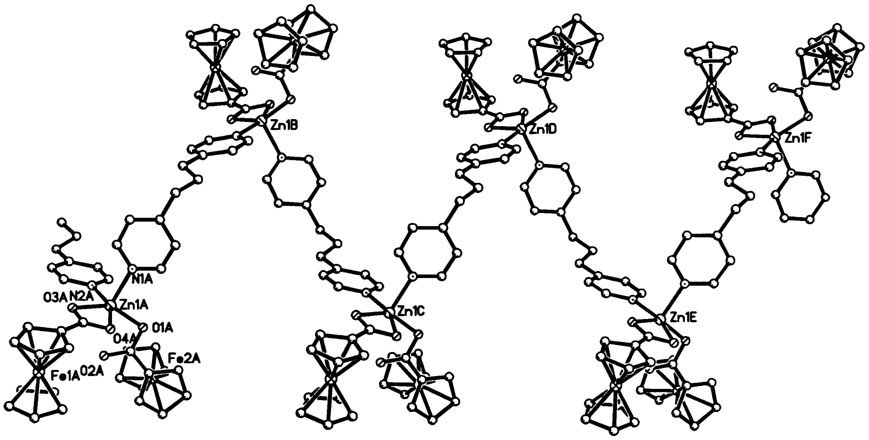

Figure 9. One-dimensional zigzag chain structure of the polymer $[Zn(FcCOO)(\eta^2\text{-}FcCOO)(bbp)]_n$.

with two terminal O atoms from different FcCOO$^-$ units and two N atoms from two bpt ligands (Figure 7). Zn atoms are inside the tetrahedron formed by the four coordinate atoms N1−O1−N4−O3. The Zn−O distances are 1.946(4) and 1.977(4) Å, respectively. And the Zn−N distances are 2.036(4) and 2.077(4) Å, respectively. Two adjacent −Zn−bpt−Zn−bpt− chains are connected by O···H−N hydrogen bonds, where O atoms are from FcCOO$^-$ units and H and N are from bpt ligands of the adjacent chain. The O···H distance is 2.095 Å. The corresponding Zn···Zn distance is 13.619 Å. Its solid state structure contains large pores with the dimensions of 10.058 × 7.821 Å^2, in which H_2O molecules can be found (Figure 8).

Crystal Structure of $[Zn(FcCOO)(\eta^2\text{-}FcCOO)(bbp)]_n$ (5). Compound **5** gives a one-dimensional zigzag chain structure (Figure 9). The coordinate modes of the FcCOO$^-$ unit are not the same as those of polymers **3** and **4**. FcCOO$^-$ units coordinate with the Zn atoms by two modes: one FcCOO$^-$ unit coordinates with one Zn atom using a terminal O atom as a monodentate ligand, while the other FcCOO$^-$ unit binds to one Zn atom as chelating bidentate ligand η^2-FcCOO$^-$. Although the organic ligands of polymers **3** and **5** are a little similar, their structures have a distinct difference. It may be that bbp is a little longer than bpe, and bbp has more flexibility than bpe. In polymer **5**, The Zn atoms are five coordinate, and they are in an axially distorted, trigonal bipyriamidal arrangement and coordinate with two O atoms of one chelating η^2-FcCOO$^-$ unit, one terminal O atom of one FcCOO$^-$ unit, and two N atoms from two bbp ligands. Atoms O3 and O4 of the η^2-FcCOO$^-$ unit and N2 of one bbp form the equatorial plane, the Zn1−N2 bond length is 2.108(2) Å, and the distances of Zn1−O3 and Zn1−O4 are 2.027(2) and 2.387(2) Å, respectively. Each Zn atom is also in the equatorial plane (the mean deviation from plane is 0.0228 Å). The O1 atom of the FcCOO$^-$ unit and N1 atom of the other bbp ligand occupy the axial position. The O1−Zn1 and Zn1−N1 bond lengths are 1.989(2) and 2.103(2) Å, respectively. All the Zn−O bond distances are longer than those of polymer **4**. The angle of O1−Zn1−N1 is 102.78(9)°. The bbp units connect all Zn atoms leading to a infinite −Zn−bbp−Zn−bbp− zigzag chain, and the Zn···Zn distance is 12.180 Å, which is shorter than the 13.619 Å distance of polymer **4**.

Both polymers **4** and **5** belong to a family of coordination polymers with ferrocene units in the side chain.

Thermogravimetric Analysis (TGA). The TG-DTA of polymers **1**−**5** was determined in the range 20−900 °C in the air. It can be seen from the TG curve that **1** loses weight from 90 to 104 °C corresponding to losses of solvent, and then it keeps losing weight from 256 to 392 °C corresponding to the decomposition of **1**. There is one weak exothermic peak at 240 °C, and there is one very strong exothermic peak at 360 °C on the DTA curve. There are two strong exothermic peaks at 320 and 348 °C on the DTA curve of polymer **2**, it keeps losing weight from 316 to 380 °C, and then a plateau region is observed from 380 to 900 °C. Two weak exothermic peaks at 252 and 384 °C and one very strong exothermic peak at 332 °C can be observed on the DTA curve of polymer **3**, it keeps losing weight from 228 to 400 °C, and then a plateau region is observed from 400 to 900 °C. We find from the TG curve that **4** loses weight from 52 to 80 °C corresponding to losses of H_2O, and then **4** decomposes from 204 to 560 °C. There is one weak endothermic peak at 206 °C (melting point), and there is one strong exothermic peak 492 °C on the DTA curve. On the DTA curve of **5**, one weak endothermic peak at 210 °C and one strong exothermic peak at 395 °C can be found, corresponding with weight loss from 200 to 425 °C in the TG curve.

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Supporting Information Available: Additional crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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