

# Preparation and structures of copper(II) and zinc(II) complexes with 5-ferrocenylpyrimidine: Structural variation derived from flexible coordination ability of the ligand and metal ions

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## Abstract

5-Ferrocenylpyrimidine (FcPM) reacts with dinuclear copper(II) carboxylates ( $[\text{Cu}_2(\text{RCOO})_4]$ ;  $\text{R} = \text{C}_6\text{H}_5$ ,  $\text{C}_5\text{H}_{11}$ ,  $\text{CH}_3$ ) to produce one-dimensional coordination polymers  $[\text{Cu}_2(\text{C}_6\text{H}_5\text{COO})_4(\text{FcPM})_n]$  (**1**),  $[\text{Cu}_2(\text{C}_5\text{H}_{11}\text{COO})_4(\text{FcPM})_n] \cdot n\text{CH}_3\text{CN}$  (**2**), and a discrete tetranuclear complex  $[\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{FcPM})_2]$  (**3**). Compounds **1** and **2** show similar zigzag chain structures, comprising alternate linking of FcPM and dinuclear copper(II) units, whereas the structure of **3** corresponds to the local structural motifs of **1** and **2**. Reaction of FcPM with zinc salts ( $\text{ZnX}_2$ ;  $\text{X} = \text{NO}_3$ ,  $\text{SCN}$ ) affords zinc-centered ferrocenyl cluster complexes,  $[\text{Zn}(\text{NO}_3)_2(\text{FcPM})_3]$  (**4**) and  $[\text{Zn}(\text{SCN})_2(\text{FcPM})_2] \cdot 0.5\text{H}_2\text{O}$  (**5**), with varying M:L ratios. FcPM acts as a bidentate ligand in **1** and **2**, and as a monodentate ligand in the others.

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**Keywords:** Coordination polymer; Polynuclear complex; Ferrocene derivative; Copper carboxylate; Zinc

## 1. Introduction

The designed construction of supramolecular coordination compounds, as prepared by the spontaneous self-assembly of metal ions and functional ligands, has received much attention in recent years [1]. In particular, construction of mixed-metal supramolecular assemblies is an important theme in modern chemistry [2]. We designed several ferrocene-based ligands and combined them with appropriate metal ions to construct mixed-metal supramolecular complexes [3]. Synthesis of ferrocene-based ligands and their molecular complexes has been studied for many years, but most of those studies use ferrocenyl-substituted carboxylates [4] and 1,1'-disubstituted ferrocenes such as 1,1'-bis(diphenylphosphino)ferrocene (dppf) [5], and the number of

mono-substituted heteroaryl ferrocenes is small [6]. Therefore, we have designed a heteroaryl-substituted ferrocene, 5-ferrocenylpyrimidine (FcPM, Chart 1) [3d], which has proven to be a highly versatile molecule for supramolecular construction. Acting as a bridging or a monodentate ligand, FcPM can produce polynuclear complexes [3c] and coordination polymers [3d]. It can even act as a hydrogen bonding acceptor to form hydrogen-bonded supramolecular assemblies [7]. This structural variety contrasts with the rather simpler complexation modes exhibited by 1,1'-disubstituted ferrocenes with heteroaryl rings such as 1,1'-di(4-pyridyl)ferrocene ( $\text{Fc}(4\text{-py})_2$ ) [8] and 1,1'-di(pyrazinyl)ferrocene ( $\text{Fc}(\text{pyz})_2$ ), which tend to produce tetranuclear metalla-macrocycles.

Appropriate choice of metal ions is a crucial factor in the directed synthesis of metal assemblies. So far, we have prepared coordination compounds of FcPM with several metal salts,  $\text{MX}_2$  ( $\text{M} = \text{Ni}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ ,  $\text{Cu}^{\text{II}}$ ;

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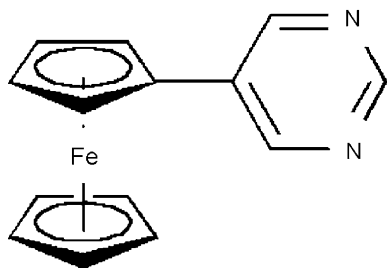


Chart 1. 5-Ferrocenylpyrimidine (FcPM).

X = SCN, NO<sub>3</sub>, CuX (X = I, Br), and M(hfac)<sub>2</sub> (hfac = hexafluoroacetylacetonate; M = Mn<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup>, Zn<sup>II</sup>) [3c, d]. The present study combines the ligand with copper(II) carboxylates and zinc(II) salts to further investigate the possibility of supramolecular construction with FcPM. The copper(II) carboxylates provide lantern- and butterfly-like di- or tetra-nuclear units to which various N-donor ligands can coordinate [9]. On the other hand, the zinc(II) ion produces a variety of coordination modes because of its *d*<sup>10</sup> electron configuration [10]. Indeed, several examples exist of interesting zinc coordination modes of ferrocenyl-carboxylates [4a,4b,4c,4d,4e]. Herein, we report the synthesis and structural characterization of coordination polymers [Cu<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>COO)<sub>4</sub>(FcPM)]<sub>n</sub> (**1**) and [Cu<sub>2</sub>(C<sub>5</sub>H<sub>11</sub>COO)<sub>4</sub>(FcPM)]<sub>n</sub> · *n*CH<sub>3</sub>CN (**2**), as well as discrete complexes [Cu<sub>2</sub>(CH<sub>3</sub>COO)<sub>4</sub>(FcPM)<sub>2</sub>] (**3**), [Zn(NO<sub>3</sub>)<sub>2</sub>(FcPM)<sub>3</sub>] (**4**), and [Zn(SCN)<sub>2</sub>(FcPM)<sub>2</sub>] · 0.5H<sub>2</sub>O (**5**).

## 2. Experimental

### 2.1. General methods

All reagents and solvents were commercially available except for FcPM [3d] and copper(II) hexanoate [9c], which were synthesized by following the literature procedure. Infrared spectra for **1–2** were recorded on a SHIMADZU Prestige-21 FTIR-8400S spectrometer attached with AIM-8800 microscope and those for **3–5** were recorded on a JASCO FT-IR 230 spectrometer as KBr pellets.

### 2.2. [Cu<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>COO)<sub>4</sub>(FcPM)]<sub>n</sub> (**1**)

Toluene (2 mL) and an acetonitrile solution (8 mL) of copper(II) benzoate (23 mg, 7.5 × 10<sup>-2</sup> mmol) were successively layered onto a toluene solution (2 mL) of FcPM (6.6 mg, 2.5 × 10<sup>-2</sup> mmol) in a test tube at room temperature. After standing for a few days, dark green crystals of **1** were formed in a 65% yield (14.2 mg). IR (cm<sup>-1</sup>): 3059 m, 1626 s, 1574 s, 1491 m, 1408 s, 1296 w, 1176 m, 1068 m, 1030 m, 843 m, 816 m, and 713 s. Anal. Found: C, 57.59; H, 3.81; N, 3.18%. Calc. for C<sub>42</sub>H<sub>32</sub>Cu<sub>2</sub>FeN<sub>2</sub>O<sub>8</sub>: C, 57.61; H, 3.68; N, 3.20%.

### 2.3. [Cu<sub>2</sub>(C<sub>5</sub>H<sub>11</sub>COO)<sub>4</sub>(FcPM)]<sub>n</sub> · *n*CH<sub>3</sub>CN (**2**)

To a solution of copper(II) hexanoate (43 mg, 15 × 10<sup>-2</sup> mmol) in acetonitrile (3 mL), a solution of FcPM (13 mg, 5.0 × 10<sup>-2</sup> mmol) in 1 mL of acetonitrile was added. After standing for a few days, dark green microcrystals of **2** were formed in a 28% yield (13 mg). IR (cm<sup>-1</sup>): 3061 m, 2930 s, 1614 s, 1585 s, 1416 s, 1315 s, 1174 m, 1107 m, 897 m, and 827 m. Results of elemental analysis indicated the loss of acetonitrile molecules from the crystal by vacuum drying. Anal. Found: C, 53.58; H, 6.63; N, 3.29%. Calc. for C<sub>38</sub>H<sub>56</sub>Cu<sub>2</sub>FeN<sub>2</sub>O<sub>8</sub> (= [Cu<sub>2</sub>(C<sub>5</sub>H<sub>11</sub>COO)<sub>4</sub>(FcPM)]<sub>n</sub>): C, 53.81; H, 6.66; N, 4.71%.

### 2.4. [Cu<sub>2</sub>(CH<sub>3</sub>COO)<sub>4</sub>(FcPM)<sub>2</sub>] (**3**)

This material was prepared as described for **2** using FcPM (13 mg, 5.0 × 10<sup>-2</sup> mmol) and copper(II) acetate (10 mg, 5.0 × 10<sup>-2</sup> mmol). After standing for a few days, dark green crystals were formed in a 63% yield (14 mg). IR (KBr, cm<sup>-1</sup>): 3086 m, 3056 w, 3027 m, 1617 s, 1562 s, 1481 s, 1428 s, 1353 s, 1293 m, 1179 m, 1052 m, 894 m, 822 m, and 683 s. Anal. Found: C, 48.51; H, 4.14; N, 6.35%. Calc. for C<sub>36</sub>H<sub>35</sub>Cu<sub>2</sub>Fe<sub>2</sub>N<sub>4</sub>O<sub>8</sub>: C, 48.56; H, 3.96; N, 6.29%.

### 2.5. [Zn(NO<sub>3</sub>)<sub>2</sub>(FcPM)<sub>3</sub>] (**4**)

To a solution of zinc(II) nitrate (5 mg, 5.0 × 10<sup>-2</sup> mmol) in methanol (2 mL), a solution of FcPM (13 mg, 5.0 × 10<sup>-2</sup> mmol) in methanol (2 mL) was added. After standing for a few days, a non-crystalline major product (50–60%) formed, together with orange crystals of **4** as a very minor product. The yield of **4** was extremely low, but this was confirmed to be a 1:3 M/L complex [Zn(NO<sub>3</sub>)<sub>2</sub>(FcPM)<sub>3</sub>] by X-ray crystallography. IR (KBr, cm<sup>-1</sup>): 3106 w, 3082 w, 1638 m, 1592 m, 1411 m, 1384 s, 1310 m, 1106 m, 1046 m, 900 m, 817 m, and 706 m. The major product seems to be a 1:1 M/L complex, [Zn(NO<sub>3</sub>)<sub>2</sub>(FcPM)] · 2H<sub>2</sub>O from elemental analysis. Anal. Found: C, 34.37; H, 3.32; N, 11.24%. Calc. for C<sub>14</sub>H<sub>16</sub>FeN<sub>4</sub>O<sub>8</sub>Zn: C, 34.35; H, 3.29; N, 11.44%.

### 2.6. [Zn(SCN)<sub>2</sub>(FcPM)<sub>2</sub>] · 0.5H<sub>2</sub>O (**5**)

This material was prepared as described for **4** using FcPM (13 mg, 5.0 × 10<sup>-2</sup> mmol) and zinc(II) thiocyanate (9 mg, 5.0 × 10<sup>-2</sup> mol). After standing for a few days, orange crystals were formed in a 46% yield (8 mg). IR (KBr, cm<sup>-1</sup>): 2924 w, 2073 s, 1593 m, 1572 s, 1482 m, 1411 m, 1178 m, 1075 m, 1001 m, 895 m, 822 s, and 706 s. Anal. Found: C, 50.33; H, 3.54; N, 11.58%. Calc. for C<sub>30</sub>H<sub>25</sub>Fe<sub>2</sub>N<sub>6</sub>O<sub>0.5</sub>S<sub>2</sub>Zn: C, 50.13; H, 3.51; N, 11.69%.

Table 1  
Crystallographic data for **1–5**

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
Empirical formula	C <sub>42</sub> H <sub>32</sub> Cu <sub>2</sub> FeN <sub>2</sub> O <sub>8</sub>	C <sub>40</sub> H <sub>59</sub> Cu <sub>2</sub> FeN <sub>3</sub> O <sub>8</sub>	C <sub>36</sub> H <sub>35</sub> Cu <sub>2</sub> Fe <sub>2</sub> N <sub>4</sub> O <sub>8</sub>	C <sub>42</sub> H <sub>36</sub> Fe <sub>3</sub> N <sub>8</sub> O <sub>6</sub> Zn	C <sub>30</sub> H <sub>25</sub> Fe <sub>2</sub> N <sub>6</sub> O <sub>0.5</sub> S <sub>2</sub> Zn
Formula weight	875.63	892.86	891.47	981.71	718.78
Crystal dimensions (mm)	0.1 × 0.1 × 0.06	0.5 × 0.3 × 0.3	0.5 × 0.5 × 0.3	0.5 × 0.5 × 0.2	0.2 × 0.2 × 0.1
Crystal system	Triclinic	Triclinic	Orthorhombic	Triclinic	Monoclinic
Space group	<i>P</i> −1	<i>P</i> −1	<i>P</i> <sub>bca</sub>	<i>P</i> −1	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	10.8149(8)	12.961(8)	13.075(14)	13.296(4)	17.1396(11)
<i>b</i> (Å)	13.8352(11)	13.587(8)	14.834(16)	13.587(4)	6.0872(4)
<i>c</i> (Å)	14.1575(11)	14.243(9)	38.97(4)	13.883(4)	29.290(2)
$\alpha$ (°)	101.553(2)	75.775(9)		61.130(4)	
$\beta$ (°)	95.110(2)	88.547(9)		66.916(5)	97.140(10)
$\gamma$ (°)	110.780(2)	65.194(10)		72.735(5)	
<i>V</i> (Å <sup>3</sup> )	1890.5(3)	2198(2)	7558(14)	2002.4(10)	3032.(3)
<i>Z</i>	2	2	8	1	4
<i>d</i> <sub>calcd.</sub> (g cm <sup>−3</sup> )	1.538	1.349	1.535	1.628	1.573
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
<i>T</i> (K)	293(2)	293(2)	293(2)	293(2)	293(2)
Absorption coefficient (mm <sup>−1</sup> )	1.550	1.334	1.918	1.717	1.899
Measured reflections	14157	10824	8509	8652	6898
Final <i>R</i> <sub>1</sub> <sup>a</sup>	0.0534	0.0810	0.0510	0.0385	0.0467
Final <i>wR</i> <sub>2</sub> <sup>b</sup>	0.0974	0.191	0.1187	0.0741	0.1265
Goodness of fit	1.008	1.003	0.998	1.020	1.040

$$^a R_1 = \sum \|F_o| - |F_c| \| / \sum |F_o|$$

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

## 2.7. X-ray diffraction studies

X-ray diffraction data for single crystals were collected on a Bruker SMART APEX CCD diffractometer equipped with a graphite crystal and incident beam monochromator using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Crystal data, data collection parameters, and analysis statistics for **1–5** are listed in Table 1. Selected bond lengths and angles are given in Tables 2 and 3. The frames were integrated by using the Siemens SAINT+ program [12], and the data were corrected for absorption by using the SADABS program [13]. The structures were solved by the direct method (SHELXS-97 [14]) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were inserted at the calculated positions and allowed to ride on their respective parent atoms, except for the water hydrogen atoms in **5**, which could not be located.

## 3. Results and discussion

### 3.1. Preparation and crystal structures of copper(II) complexes with FcPM

Three copper(II) complexes – [Cu<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>COO)<sub>4</sub>(FcPM)]<sub>*n*</sub> (**1**), [Cu<sub>2</sub>(C<sub>5</sub>H<sub>11</sub>COO)<sub>4</sub>(FcPM)]<sub>*n*</sub> · *n*CH<sub>3</sub>CN (**2**), and [Cu<sub>2</sub>(CH<sub>3</sub>COO)<sub>4</sub>(FcPM)<sub>2</sub>] (**3**) – were obtained as air-stable green crystals by the reaction of the corre-

sponding dinuclear copper(II) carboxylates with FcPM in acetonitrile. These complexes gave rise to markedly different architectures: one-dimensional polymeric structures for **1** and **2**, and a discrete tetranuclear structure for **3**. Their structural formulas are shown in Fig. 1. In these compounds, FcPM coordinates to the apical sites of the dinuclear lantern units. The IR spectra of these complexes showed strong bands at around 1620 and 1420 cm<sup>−1</sup>, which are characteristic of  $\nu(\text{COO})$  in the dinuclear units [9,11].

In the crystals of **1** and **2**, the dinuclear units [Cu<sub>2</sub>(R-COO)<sub>4</sub>] (R = C<sub>6</sub>H<sub>5</sub>, C<sub>5</sub>H<sub>11</sub>) are bridged by FcPM ligands to form a *side-chain* coordination polymer with ferrocenyl pendants. The one-dimensional chain structures of **1** and **2**, as determined by crystallographic analyses, are shown respectively in Figs. 2(a) and (b). The extended structures closely resemble each other: in both complexes, the chains run along the [0 1 1] direction, with the shortest interchain Cu ··· Cu distances being ca. 10 Å. The shortest intrachain and interchain Fe ··· Fe distances in **1** are ca. 15.1 and 7.0 Å, respectively, and those in **2** are ca. 15.8 and 7.0 Å, respectively. In complex **2**, two alkyl chains in each paddle wheel unit show bent structures with a partial *cis* conformation, whereas the other two chains adopt the all *trans* conformation and show straight structures, perhaps because of packing effects.

An ORTEP [15] drawing of the local structure of **1** with the numbering scheme is shown in Fig. 3. The structure of **2** closely resembles that of **1**. Each complex

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

<b>1</b>			
<i>Bond lengths</i>			
Cu1–O1	1.961(3)	Cu1–O2	1.966(2)
Cu1–O3	1.945(3)	Cu1–O4	1.960(2)
Cu1–N1	2.192(3)	Cu2–O5	1.966(2)
Cu2–O6	1.976(3)	Cu2–O7	1.958(2)
Cu2–O8	1.969(3)	Cu2–N2	2.184(3)
<i>Bond angles</i>			
O1–Cu1–O2	87.8(1)	O1–Cu1–O3	169.2(1)
O1–Cu1–O4	90.9(1)	O1–Cu1–N1	93.9(1)
O2–Cu1–O3	90.7(1)	O2–Cu1–O4	169.1(1)
O2–Cu1–N1	91.0(1)	O3–Cu1–O4	88.5(1)
O3–Cu1–N1	96.9(1)	O4–Cu1–N1	99.9(1)
O5–Cu2–O6	88.4(1)	O5–Cu2–O7	169.1(1)
O5–Cu2–O8	90.1(1)	O5–Cu2–N2	93.8(1)
O6–Cu2–O7	90.9(1)	O6–Cu2–O8	169.2(1)
O6–Cu2–N2	92.2(1)	O7–Cu2–O8	88.5(1)
O7–Cu2–N2	97.1(1)	O8–Cu2–N2	98.6(1)
<b>2</b>			
<i>Bond lengths</i>			
Cu1–O1	1.962(6)	Cu1–O2	1.971(5)
Cu1–O3	1.937(7)	Cu1–O4	1.959(6)
Cu1–N1	2.209(7)	Cu2–O5	1.974(6)
Cu2–O6	1.960(8)	Cu2–O7	1.958(6)
Cu2–O8	1.928(8)	Cu2–N2	2.196(6)
<i>Bond angles</i>			
O1–Cu1–O2	91.3(2)	O1–Cu1–O3	170.5(2)
O1–Cu1–O4	88.8(3)	O1–Cu1–N1	91.2(2)
O2–Cu1–O3	88.2(3)	O2–Cu1–O4	168.7(3)
O2–Cu1–N1	93.3(2)	O3–Cu1–O4	89.8(3)
O3–Cu1–N1	98.3(2)	O4–Cu1–N1	89.0(3)
O5–Cu2–O6	92.1(3)	O5–Cu2–O7	169.2(2)
O5–Cu2–O8	88.4(3)	O5–Cu2–N2	93.5(2)
O6–Cu2–O7	87.5(3)	O6–Cu2–O8	169.5(3)
O6–Cu2–N2	93.3(3)	O7–Cu2–O8	90.0(3)
O7–Cu2–N2	97.4(2)	O8–Cu2–N2	96.1(3)

has two kinds of crystallographically independent copper(II) lantern units, each sitting on the center of symmetry. Copper(II) ions are surrounded by an N-donor nitrogen atom and four carboxylate oxygen atoms to form a distorted square pyramidal geometry; the Cu–N bond lengths of ca. 2.20 Å are slightly longer than typical values (2.0–2.1 Å) as a result of Jahn–Teller distortion of the copper(II) ion. The intrachain Cu1...Cu1\* and Cu2...Cu2\* distances via the carboxylate bridge in **1** are 2.6035(6) and 2.6029(6) Å, respectively; those in **2** are 2.606(2) and 2.605(2) Å, respectively. These values are comparable to those that are usually found in carboxylate-bridged dinuclear copper(II) complexes [9]. The Cu1...Cu2 distances via the bridging ligand of ca. 6.2 Å in both compounds are also typical values for pyrimidine complexes [15]. Dihedral angles between the pyrimidine (PM) ring and cyclopentadienyl (Cp) ring of **1** and **2** are 8.8(2)° and 2.1(5)°, respectively, the latter being nearly co-planar.

On the other hand, complex **3** is a discrete complex, not a coordination polymer. An ORTEP drawing of

Table 3  
Selected bond lengths (Å) and bond angles (°) for **3–5**

<b>3</b>			
<i>Bond lengths</i>			
Cu1–O1	2.001(3)	Cu1–O3	1.982(3)
Cu1–O5	2.004(3)	Cu1–O7	1.986(3)
Cu1–N1	2.224(4)	Cu2–O2	1.981(3)
Cu2–O4	1.976(4)	Cu2–O6	1.983(3)
Cu2–O8	1.996(3)	Cu2–N3	2.228(4)
<i>Bond angles</i>			
O1–Cu–O3	90.4(2)	O1–Cu–O5	167.1(1)
O1–Cu–O7	89.2(2)	O1–Cu–N1	97.6(1)
O3–Cu–O5	90.5(2)	O3–Cu–O7	169.4(1)
O3–Cu–N1	92.6(1)	O5–Cu–O7	87.5(2)
O5–Cu–N1	95.2(1)	O7–Cu–N1	98.0(1)
O2–Cu–O4	89.8(2)	O2–Cu–O6	170.3(1)
O2–Cu–O8	91.0(2)	O2–Cu–N3	96.7(2)
O4–Cu–O6	89.8(2)	O4–Cu–O8	168.2(1)
O4–Cu–N3	97.1(1)	O6–Cu–O8	87.4(2)
O6–Cu–N3	93.0(2)	O8–Cu–N3	94.5(1)
<b>4</b>			
<i>Bond lengths</i>			
Zn–O1	2.110(2)	Zn–O4	2.134(2)
Zn–N1	2.131(2)	Zn–N3	2.142(2)
Zn–O5	2.148(2)		
<i>Bond angles</i>			
O1–Zn–N1	90.4(1)	O1–Zn–N3	87.3(1)
O1–Zn–O5	88.3(1)	O1–Zn–O4	175.6(1)
O4–Zn–N1	94.0(1)	O4–Zn–N3	92.9(1)
O4–Zn–O5	90.3(1)	N1–Zn–N3	94.9(1)
N1–Zn–O5	100.4(1)	N3–Zn–O5	164.1(1)
<b>5</b>			
<i>Bond lengths</i>			
Zn–N1	2.045(3)	Zn–N3	2.025(3)
Zn–N5	1.915(4)	Zn–N6	1.913(3)
<i>Bond angles</i>			
N1–Zn–N3	104.5(1)	N1–Zn–N5	101.0(1)
N1–Zn–N6	109.9(1)	N3–Zn–N5	112.1(1)
N3–Zn–N6	112.7(1)	N5–Zn–N6	115.3(2)

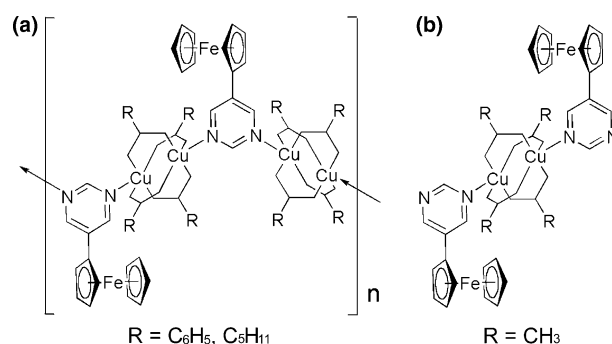


Fig. 1. Structural formulas of (a) **1** and **2**, and (b) **3**.

the tetranuclear complex is shown in Fig. 4(a). In this complex, the paddle wheel unit [Cu<sub>2</sub>(CH<sub>3</sub>COO)<sub>4</sub>] is coordinated with two FcPM ligands in a monodentate fashion. The dihedral angles between the PM ring and Cp ring in **3** are 44.5(2)° and 21.4(2)° for FcPM with



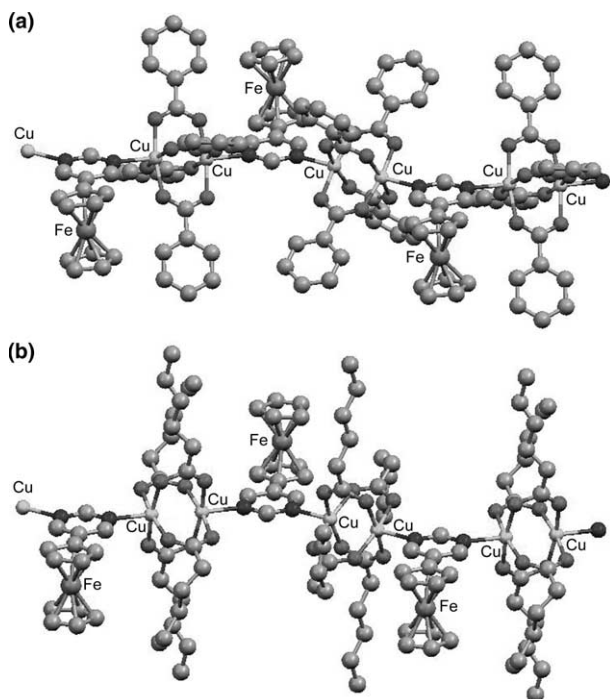


Fig. 2. One-dimensional chain structures of (a) **1** and (b) **2**. Hydrogen atoms are omitted for clarity.

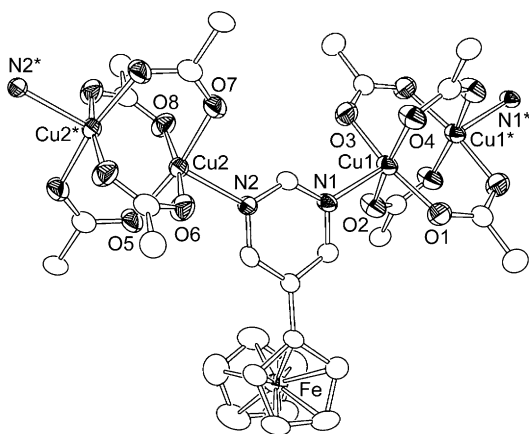


Fig. 3. ORTEP drawing (30% thermal probability ellipsoids) of the one-dimensional chain complex **1**. Alkyl chains and hydrogen atoms are omitted for clarity.

Fe1 and FcPM with Fe2, respectively. This difference may originate from packing effects. The copper(II) ions in **3** also adopt a distorted square pyramidal coordination geometry in which Jahn–Teller distortion elongates the Cu–N bond length (2.2 Å). The intramolecular Cu...Cu distance is 2.648(2) Å. Fig. 4(b) shows the existence of intermolecular  $\pi$ – $\pi$  interactions between the adjacent ligands, constructing a dimer-like structure in the crystal. The centroid–centroid distance between the PM rings is ca. 3.59 Å. The smallest intra- and intermolecular Fe...Fe distances in **3** are ca. 15.8 and 6.6 Å, respectively. The smallest intermolecular Cu...Cu distance is ca. 7.4 Å.

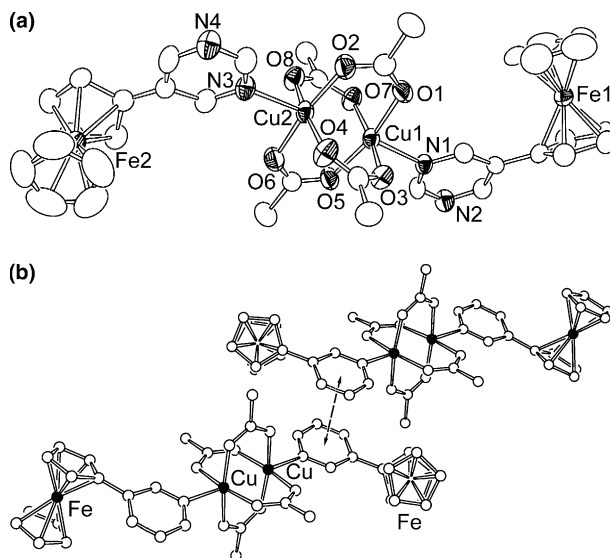


Fig. 4. (a) ORTEP drawing (50% thermal probability ellipsoids) of the tetranuclear complex **3**. (b) Intermolecular  $\pi$ – $\pi$  interaction between adjacent ligands in **3**. Hydrogen atoms are omitted for clarity.

Results for **1** and **2** indicate that the coordination polymer structures are maintained for carboxylates with larger substituents, as seen in Figs. 2(a) and (b). The substituents fill the space between the ferrocenyl groups within the chain, leading to efficient packing of the straight chain structures in the crystals. On the other hand, as observed for **3**, copper acetate afforded no coordination polymers. The difference probably results from steric effects; considering the packing structures of **1** and **2**, a coordination polymer with a small substituent on the carboxylate would be difficult to pack into crystals. Substituents' electronic effects may be less important, considering the comparable  $pK_a$  values of carboxylates in **2** and **3**. It is noteworthy that the structure of **3** can be regarded as a local structure or a building motif of the coordination polymers **1** and **2**. An analogous phenomenon has been found in the case of  $M(\text{hfac})_2$  complexes with FcPM; both coordination polymers  $[M(\text{hfac})_2(\text{FcPM})]_n$  and molecular complexes  $[M(\text{hfac})_2(\text{FcPM})_2]$  can be formed, the latter being regarded as the structural motif of the former [3c,3d]. In the  $M(\text{hfac})_2$  complexes, the products can be converted mutually or isolated selectively by careful choice of the reaction conditions. Nevertheless, in this particular case, changing the reaction conditions or the starting materials ratio did not affect the stoichiometry or the product structures. Therefore, the bulkiness of the carboxylates resulted in the stabilization of different structures.

### 3.2. Preparation and crystal structures of zinc(II) complexes with FcPM

Two zinc complexes,  $[\text{Zn}(\text{NO}_3)_2(\text{FcPM})_3]$  (**4**) and  $[\text{Zn}(\text{SCN})_2(\text{FcPM})_2] \cdot 0.5\text{H}_2\text{O}$  (**5**), were obtained as

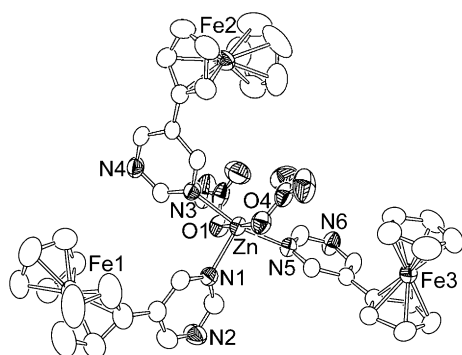


Fig. 5. ORTEP drawings (50% thermal probability ellipsoids) of the tetranuclear complex **4**. Hydrogen atoms are omitted for clarity.

air-stable orange crystals by reaction of the corresponding zinc salts and FcPM in methanol. For **4**, however, the yield was extremely low. Elemental analysis suggested that the major product was  $[\text{Zn}(\text{NO}_3)_2(\text{FcPM})] \cdot 2\text{H}_2\text{O}$ . Complexes **4** and **5** can be regarded as zinc-centered ferrocenyl cluster complexes, in which FcPM acts as a monodentate ligand.

ORTEP drawings of these multinuclear complexes are shown respectively in Figs. 5 and 6. Compound **4**, composed of  $\text{Zn}(\text{NO}_3)_2$  and three FcPM ligands, is a tetranuclear mixed-metal complex. This complex was found to be isostructural with the copper(II) analogue,  $[\text{Cu}(\text{NO}_3)_2(\text{FcPM})_3]$  [3d]. The unit cell volume of **4** is slightly larger than that of the copper complex, reflecting the larger ionic radius of the zinc ion. The zinc ion is coordinated by three N-donor nitrogen atoms and two nitrate oxygen atoms to form a distorted square pyramidal geometry. The Zn–N and Zn–O bond lengths are in the normal range of 2.0–2.2 Å. The intramolecular Fe1...Fe2, Fe2...Fe3, and Fe3...Fe1 distances are ca. 9.8, 9.9, and 11.9 Å, respectively. On the other hand, compound **5** is a trinuclear complex consisting of  $\text{Zn}(\text{SCN})_2$  and two FcPM ligands. The coordination geometry around the metal center of **5** is a four-coordinate tetrahedral. The Zn–N bond lengths with thiocyanate nitrogen (ca. 1.91 Å) are shorter than those with FcPM nitrogen (ca. 2.0 Å). This tendency was evident in similar compounds,  $[\text{M}(\text{SCN})_2(\text{FcPM})_4]$  (M = Ni, Co) [3d]. The two FcPM ligands differ in their dihedral angles between the Cp ring and the pyrimidine ring; the angle for FcPM with Fe1 is  $0.6(2)^\circ$ , whereas that for FcPM with Fe2 is  $25.5(2)^\circ$ . Fig. 6(b) shows that the planar conformation around the former ligand is probably caused by  $\pi$ – $\pi$  interaction between adjacent FcPM molecules (ca. 3.58 Å from centroid to centroid). The crystal of **5** accommodates waters of crystallization between the trinuclear units.

It is noteworthy that variation of the L:M ratio, being 1:3 and 1:2 for **4** and **5**, respectively, was achieved for the same metal ion through the appropriate choice of the counter anions. A related phenomenon was revealed in the complexes of copper(II) ions,  $[\text{Cu}(\text{NO}_3)_2(\text{FcPM})_3]$

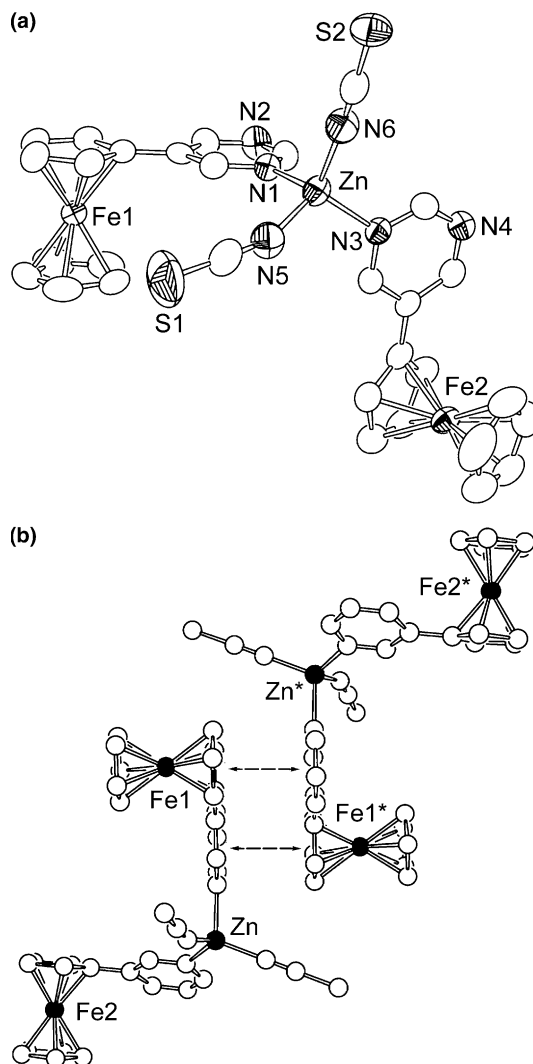


Fig. 6. (a) ORTEP drawing (50% thermal probability ellipsoids) of the trinuclear complex **5**. (b) Intermolecular  $\pi$ – $\pi$  interactions between adjacent ligands in **5**. Solvent molecules and hydrogen atoms are omitted for clarity.

and  $[\text{Cu}(\text{NO}_3)_2(\text{ferrocenylpyrazine})_2]$  [3d]. They exhibit different M:L stoichiometries even though the ligands are similar. These phenomena are ascribable to the flexible coordination characteristics of both zinc(II) [10] and copper(II) ions. It is noteworthy that, in contrast to the zinc complexes of FcPM, those of ferrocenyl-carboxylates afford not only molecular complexes, but also a variety of coordination polymers [4d]. A partial explanation is that FcPM is a neutral ligand and the zinc ions are coordinated also by its counter anions, whereas the carboxylates can form network structures in the absence of such counter anions.

#### 4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic

Data Centre, CCDC Nos. 255025 and 245078–245081 for compounds **1** and **2–5**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC12, Union Road, Cambridge CB2 1EZ, UK (Fax. +44(1223)336-033; deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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