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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 ($[Cu_2(RCOO)_4]$; R = C_6H_5, C_5H_{11}, CH_3) to produce one-dimensional coordination polymers $[Cu_2(C_6H_5COO)_4(FcPM)]_n$ (**1**), $[Cu_2(C_5H_{11}COO)_4(FcPM)]_n \cdot nCH_3CN$ (**2**), and a discrete tetranuclear complex $[Cu_2(CH_3COO)_4(FcPM)_2]$ (**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 (ZnX_2; X = NO_3, SCN) affords zinc-centered ferrocenyl cluster complexes, $[Zn(NO_3)_2(FcPM)_3]$ (**4**) and $[Zn(SCN)_2(FcPM)_2] \cdot 0.5H_2O$ (**5**), with varying M:L ratios. FcPM acts as a bidentate ligand in **1** and **2**, and as a monodentate ligand in the others.

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 ($Fc(4\text{-}py)_2$) [8] and 1,1′-di(pyrazinyl)ferrocene ($Fc(pyz)_2$), 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, MX_2 ($M = Ni^{II}$, Co^{II}, Cu^{II};

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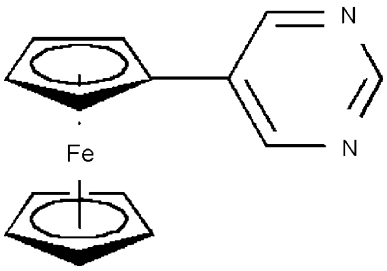

Chart 1. 5-Ferrocenylpyrimidine (FcPM).

X = SCN, NO_3), CuX (X = I, Br), and $M(hfac)_2$ (hfac = hexafluoroacetylacetonate; M = Mn^{II}, Ni^{II}, Cu^{II}, Zn^{II}) [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^{10} electron configuration [10]. Indeed, several examples exist of interesting zinc coordination complexes of ferrocenylcarboxylates [4a,4b,4c,4d,4e]. Herein, we report the synthesis and structural characterization of coordination polymers $[Cu_2(C_6H_5COO)_4(FcPM)]_n$ (**1**) and $[Cu_2(C_5H_{11}COO)_4(FcPM)]_n \cdot nCH_3CN$ (**2**), as well as discrete complexes $[Cu_2(CH_3COO)_4(FcPM)_2]$ (**3**), $[Zn(NO_3)_2(FcPM)_3]$ (**4**), and $[Zn(SCN)_2(FcPM)_2] \cdot 0.5H_2O$ (**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. $[Cu_2(C_6H_5COO)_4(FcPM)]_n$ (1)

Toluene (2 mL) and an acetonitrile solution (8 mL) of copper(II) benzoate (23 mg, 7.5×10^{-2} mmol) were successively layered onto a toluene solution (2 mL) of FcPM (6.6 mg, 2.5×10^{-2} 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^{-1}): 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 $C_{42}H_{32}Cu_2FeN_2O_8$: C, 57.61; H, 3.68; N, 3.20%.

2.3. $[Cu_2(C_5H_{11}COO)_4(FcPM)]_n \cdot nCH_3CN$ (2)

To a solution of copper(II) hexanoate (43 mg, 15×10^{-2} mmol) in acetonitrile (3 mL), a solution of FcPM (13 mg, 5.0×10^{-2} 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^{-1}): 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 $C_{38}H_{56}Cu_2FeN_2O_8$ (= $[Cu_2(C_5H_{11}COO)_4(FcPM)]_n$): C, 53.81; H, 6.66; N, 4.71%.

2.4. $[Cu_2(CH_3COO)_4(FcPM)_2]$ (3)

This material was prepared as described for **2** using FcPM (13 mg, 5.0×10^{-2} mmol) and copper(II) acetate (10 mg, 5.0×10^{-2} mmol). After standing for a few days, dark green crystals were formed in a 63% yield (14 mg). IR (KBr, cm^{-1}): 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 $C_{36}H_{35}Cu_2Fe_2N_4O_8$: C, 48.56; H, 3.96; N, 6.29%.

2.5. $[Zn(NO_3)_2(FcPM)_3]$ (4)

To a solution of zinc(II) nitrate (5 mg, 5.0×10^{-2} mmol) in methanol (2 mL), a solution of FcPM (13 mg, 5.0×10^{-2} 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 $[Zn(NO_3)_2(FcPM)_3]$ by X-ray crystallography. IR (KBr, cm^{-1}): 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 be a 1:1 M/L complex, $[Zn(NO_3)_2(FcPM)] \cdot 2H_2O$ from elemental analysis. Anal. Found: C, 34.37; H, 3.32; N, 11.24%. Calc. for $C_{14}H_{16}FeN_4O_8Zn$: C, 34.35; H, 3.29; N, 11.44%.

2.6. $[Zn(SCN)_2(FcPM)_2] \cdot 0.5H_2O$ (5)

This material was prepared as described for **4** using FcPM (13 mg, 5.0×10^{-2} mmol) and zinc(II) thiocyanate (9 mg, 5.0×10^{-2} mol). After standing for a few days, orange crystals were formed in a 46% yield (8 mg). IR (KBr, cm^{-1}): 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 $C_{30}H_{25}Fe_2N_6O_{0.5}S_2Zn$: C, 50.13; H, 3.51; N, 11.69%.