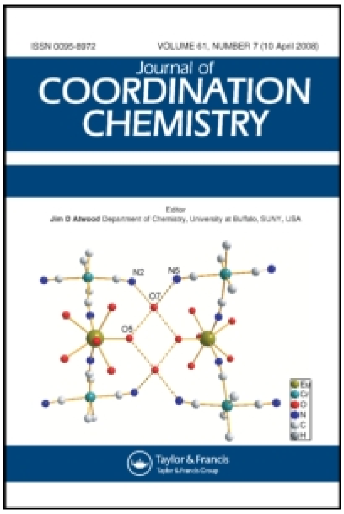

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Synthesis and structures of three heterobimetallic compounds based on a new ferrocenyl pyridine ligand

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The reactions of 2-PAMF with metal perchlorates [2-PAMF = (2-pyridylmethylamino)carbonylferrocene] yielded three coordination compounds, $M(2\text{-PAMF})_2(CH_3CH_2OH)_2(ClO_4)_2$ (M = Co **1**, Zn **2**, and Cu **3**), which were characterized by single crystal X-ray diffraction and IR spectroscopy. Compounds **1** and **2** have similar structures with six-coordinate metals in octahedral geometries. The CuII in **3** possesses a severely distorted octahedral geometry due to Jahn–Teller distortion. Adjacent molecules in the three compounds were linked by intermolecular hydrogen bonds to form a 1-D supramolecular chain.

Keywords: Ferrocene; Pyridine-amide ligand; Crystal structures

1. Introduction

Ferrocene and its derivatives have been extensively studied since isolation by Kealy and Pauson more than 50 years ago [1]. A large number of ferrocene-based ligands have been exploited to produce multimetal-containing complexes for potential applications in homogeneous catalysis [2], electrochemical sensing [3], material science [4, 5], and nonlinear optical materials [6, 7]. Pyridylmethylamide ligands have been explored due to their ability to pre-organize and tune structural properties of their transition metal complexes [8–11]. Pyridylmethylamidoacyl groups with three potential donors, the N and the O from the amide and the N from pyridyl, may chelate metal ions to generate flexible assemblies. The pyridylmethylamide group may also contribute to the construction of supramolecular assemblies by forming hydrogen bonds using its amino groups and π–π stacking interactions of pyridyl rings. A series of high-nuclear copper complexes bearing the pyridylmethylamide group have been reported by Houser and his coworkers [12–15]. The coordination geometry of the central metal is substantially influenced by the steric effect of the substituents of the amide, the use of base and even the starting materials [16]. We attempted to combine the

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ferroceneformyl and pyridylmethylamide to synthesize a new ligand whose metal complexes may possess the unique characteristics of ferrocene and structures tuned by the bulky ferrocene group on the amide.

Herein, we introduce a ferrocenylformyl group into 2-amino methyl pyridine to get a multidentate organometallic ligand [2-PAMF = (2-pyridylmethylamino)-carbonylferrocene] bearing a flexible spacer as the "building unit" of the desired products.

Reactions of 2-PAMF with metal perchlorates led to the isolation of three new mononuclear compounds, in which 2-PAMF chelates the metal to form a seven-membered ring. Mononuclear molecules are further connected to form a 1-D chain via hydrogen bonds.

2. Experimental

2.1. *Materials and methods*

All chemicals were commercially purchased, were of analytical reagent grade, and used without purification. The IR spectra were recorded in the range 4000–400 cm^{-1} on a Perkin–Elmer PE Spectrum One FT/IR spectrometer using KBr pellets. Elemental analyses (C, H, and N) were performed on a Perkin–Elmer PE 2400 II CHN elemental analyzer.

2.2. *Synthesis*

2.2.1. 2-PAMF. 1-Chlorocarbonylferrocene, prepared by literature methods [17] (3.7 g, 15 mmol), was dissolved in dry CH_2Cl_2 (40 mL) and added dropwise under nitrogen to a stirred mixture of 2-(aminomethyl)pyridine (1.55 mL, 15 mmol) and triethylamine (2.1 mL, 15 mmol) in dry CH_2Cl_2 (30 mL) at 0°C. The mixture was stirred at 0°C for 7 h and at room temperature for 16 h. Saturated $NaHCO_3$ aqueous solution (40 mL) was added and the mixture was extracted with CH_2Cl_2 (3×30 mL). The deep red solution was dried over $MgSO_4$, filtered, and solvent was removed under reduced pressure to give a red-brown solid. The compound was recrystallized from a mixture of MeOH and H_2O to give deep orange needles. Yield, 63%. IR (KBr pellet, cm^{-1}): 3317 vs (ν N–H), 1634 s (ν C=O), 1545 vs (ν C=C), 1308 m (δ N–H), 483 m (ring tilt of Fe–Cp). Anal. Calcd for $C_{17}H_{16}N_2OFe$ (%): C, 63.77; H, 5.04; N, 8.75. Found: C, 63.99; H, 5.02; N, 8.48.

2.2.2. $Co(2\text{-}PAMF)_2(CH_3CH_2OH)_2(ClO_4)_2$ (1). A solution of 2-PAMF (0.065 g, 0.2 mmol) in ethanol (10 mL) was slowly added to a solution of $Co(ClO_4)_2 \cdot 6H_2O$ (0.073 g, 0.2 mmol) in ethanol (10 mL). The resulting solution stood at room temperature in the dark for 24 h giving dark red crystals suitable for X-ray single crystal analysis (42% yield). IR (KBr pellet, cm^{-1}): 3376 vs (ν N–H), 1607 s (ν C=O), 1585 vs (ν C=C), 1309 m (δ N–H), 1107 s (ν Cl–O), 497 m (ring tilt of Fe–Cp). Anal. Calcd for $C_{38}H_{44}Cl_2CoFe_2N_4O_{12}$ (%): C, 46.09; H, 4.48; N, 5.66. Found: C, 45.92; H, 4.41; N, 5.83.

2.2.3. $Zn(2\text{-PAMF})_2(CH_3CH_2OH)_2(ClO_4)_2$ (2). A solution of 2-PAMF (0.0643 g, 0.2 mmol) in isopropanol (10 mL) was slowly added to a solution of $Zn(ClO_4)_2 \cdot 6H_2O$ (0.0745 g, 0.2 mmol) in ethanol (10 mL). The resulting solution was allowed to stand at room temperature in the dark. Red-brown crystals suitable for X-ray single crystal analysis were obtained in 24 h (51% yield). IR (KBr pellet, cm^{-1}): 3348 vs (ν N–H), 1604 s (ν C=O), 1596 vs (ν C=C), 1311 m (δ N–H), 1107 s (ν Cl–O), 489 m (ring tilt of Fe–Cp). Anal. Calcd for $C_{38}H_{44}Cl_2ZnFe_2N_4O_{12}$ (%): C, 45.79; H, 4.45; N, 5.62. Found: C, 46.03; H, 4.49; N, 5.74.

2.2.4. $Cu(2\text{-PAMF})_2(CH_3CH_2OH)_2(ClO_4)_2$ (3). A solution of 2-PAMF (0.065 g, 0.2 mmol) in isopropanol (10 mL) was slowly added to a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.074 g, 0.2 mmol) in ethanol (10 mL). The resulting solution stood at room temperature in the dark for 3 days giving red-brown crystals suitable for X-ray single crystal analysis (46% yield). IR (KBr pellet, cm^{-1}): 3446 vs (ν N–H), 1611 s (ν C=O), 1571 vs (ν C=C), 1312 m (δ N–H), 1108 s (ν Cl–O), 499 m (ring tilt of Fe–Cp). Anal. Calcd for $C_{38}H_{44}Cl_2CuFe_2N_4O_{12}$ (%): C, 45.87; H, 4.46; N, 5.63. Found: C, 44.95; H, 4.21; N, 5.89.

2.3. *X-ray measurements*

X-ray diffraction studies on **1**–**3** were performed at 298(2) K using a Bruker CCD Area Detector with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods [18] and refined using full-matrix least-squares based on F^2 with all nonhydrogen atoms anisotropic; hydrogens were included on calculated positions, riding on their carriers. All calculations were done with SHELX-97 [19]. Further details are given in table 1, with selected bond lengths and angles in table 2.

3. Results and discussions

3.1. *Synthesis*

Ligand 2-PAMF was prepared by reaction of chlorocarbonylferrocene with 2-(aminomethyl)pyridine in dry CH_2Cl_2. The complexes were synthesized by reaction of 2-PAMF with metal perchlorate hexahydrates, $M(ClO_4)_2 \cdot 6H_2O$ (M = Co, Zn, and Cu). Ferrocene derivatives bearing electron-withdrawing groups undergo photolysis in some solvents to cause cleavage of both ring-metal and ring-carbonyl, giving free Fe^{2+} cation and free radicals [20–23]. Thus, all procedures should be performed in the dark. When the reaction was carried out in light, deep brown precipitate was produced, which could not be identified. It is presumed that the ferrocenyl ligands undergo photolysis and cause a series of subsequent reactions [6].

3.2. *IR spectroscopy*

Compounds **1**–**3** have very similar IR spectra in the range 4000–400 cm^{-1}. Bands attributable to ν(N–H) occur at 3376 cm^{-1} for **1**, 3348 cm^{-1} for **2** and 3446 cm^{-1} for **3**, slightly red-shifted compared with the ligand (3317 cm^{-1}) indicating coordination of the –NH. Strong absorption bands around 1604 and 1611 cm^{-1} for **1**–**3** can be assigned to ν(C=O), blue-shifted compared to the ligand (1634 cm^{-1}), indicating coordination of the carbonyl. The characteristic IR bands around 3100 and 490 cm^{-1} due to ν(C–H) and ν(Fe–Cp) vibrations are close to previously reported compounds [24].

Table 1. Crystal data and structure refinement for **1**–**3**.

	1	**2**	**3**
Chemical formula	$C_{38}H_{44}Cl_2CoFe_2N_4O_{12}$	$C_{38}H_{44}Cl_2ZnFe_2N_4O_{12}$	$C_{38}H_{44}Cl_2CuFe_2N_4O_{12}$
Formula weight	990.30	996.74	994.91
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
Unit cell dimensions (Å, °)			
a	10.737(7)	10.766(3)	8.621(3)
b	20.877(13)	20.822(6)	10.076(4)
c	10.402(6)	10.437(3)	24.140(8)
α	90	90	90
β	117.436(7)	117.462(4)	99.220(4)
γ	90	90	90
V (Å^3)	2069(2)	2076.0(10)	2069.8(13)
Density (Calcd) (Mg m^{-3})	1.589	1.595	1.596
Absorption coefficient (mm^{-1})	1.283	1.458	1.396
θ range for data collection (°)	2.14–25.01	1.96–25.01	1.71–25.01
F(000)	1018	1024	1022
Reflections collected	10,335	10,575	10,273
Unique reflections	3581 [R(int) = 0.0886]	3655 [R(int) = 0.0689]	3636 [R(int) = 0.0669]
Parameters	268	268	306
Goodness-of-fit on F^2	1.022	1.054	1.027
R_1 [$I > 2\sigma(I)$]	0.0483	0.0460	0.0497
wR_2 (all data)	0.1383	0.1259	0.1422
Largest diff. peak and hole (e Å^{-3})	0.545, −0.316	0.519, −0.435	0.434, −0.505

Table 2. Selected bond lengths (Å) and angles (°) for **1**–**3**.

1			
Co(1)–O(1)	2.093(3)	O(1)–Co(1)–N(2)	93.16(13)
Co(1)–O(2)	2.132(3)	O(1A)–Co(1)–N(2)	86.84(13)
Co(1)–N(2)	2.153(4)	O(1)–Co(1)–O(2)	87.18(14)
O(1)–Co(1)–O(1A)	180.00(15)	O(1A)–Co(1)–O(2)	92.82(14)
O(2)–Cu(1)–O(2A)	180.000(1)	N(2)–Co(1)–O(2)	86.29(14)
O(2A)–Co(1)–O(2)	180.0	N(2A)–Co(1)–O(2)	93.71(14)
2			
Zn(1)–O(1)	2.116(3)	O(1)–Zn(1)–N(2)	92.97(14)
Zn(1)–O(2)	2.191(4)	O(1A)–Zn(1)–N(2)	87.03(14)
Zn(1)–N(2)	2.127(4)	O(1)–Zn(1)–O(2)	86.73(14)
O(1)–Zn(1)–O(1A)	180.00(16)	O(1A)–Zn(1)–O(2)	93.27(14)
N(2)–Zn(1)–N(2A)	180.0	N(2)–Zn(1)–O(2)	86.25(15)
O(2)–Zn(1)–O(2A)	180.0(2)	N(2A)–Zn(1)–O(2)	93.75(15)
3			
Cu(1)–O(1)	2.004(3)	N(2)–Cu(1)–O(1)	93.29(14)
Cu(1)–N(2)	1.993(4)	N(2)–Cu(1)–O(1A)	86.71(14)
O(1)–Cu(1)–O(1A)	180.00(9)	N(2)–Cu(1)–N(2A)	180.00(17)

Note: Symmetry codes: A $-x+1$, $-y+1$, $-z+1$.

3.3. *Description of the structures*

X-ray diffraction demonstrates that **1–3** have similar structures, all crystallized in monoclinic space group *P2₁/c*. In **1** and **2**, the metal center is octahedral with two nitrogens and two oxygens from two 2-PAMF ligands in the equatorial plane [Co(1)–O(1) 2.093(3) Å, Co(1)–N(2) 2.153(4) Å for **1** and Zn(1)–O(1) 2.116(3) Å, Zn(1)–N(2) 2.127(4) Å for **2**] and two oxygens from two ethanol molecules in axial positions [Co(1)–O(2) 2.132(3) Å for **1** and Zn(1)–O(2) 2.191(4) Å for **2**], as shown in figure 1(a) and (b). The bond lengths are standard for octahedral cobalt and zinc complexes [25].

Compound **3** has almost the same structure as **1** and **2**, except that the central copper(II) has a severely distorted octahedral environment. The bond length [2.618(0) Å] of Cu(1)–O(2) is much longer than the other [Cu(1)–N(2) 1.993(4) Å and Cu(1)–O(1) 2.004(3) Å] bonds, due to Jahn–Teller distortion [26]. Distances in the equatorial plane are in normal range for octahedral copper complexes (figure 1).

The average Fe–C_{ring} distances for **1**, **2**, and **3** are 2.020(0), 2.022(7), and 2.032(4) Å, respectively, which are close to 2.04 Å of free ferrocene. The average C–C bond length and C–C–C angle of cyclopentadienyl in **1**, **2**, and **3** are 1.391(8), 1.393(9), and 1.405(1) Å and 107.996(2), 107.996(0), and 107.996(9)°, similar to those reported in [27, 28]. The cyclopentadienyl rings are perfectly planar and nearly parallel with the dihedral angle of 1.844(0)° for **1**, 1.845(14)° for **2**, and 1.538(3)° for **3**.

Each ClO_4^- in the three compounds forms intermolecular hydrogen bonds (table 3) O···H–O and O···H–N with the amino group and hydroxyl group of coordinated

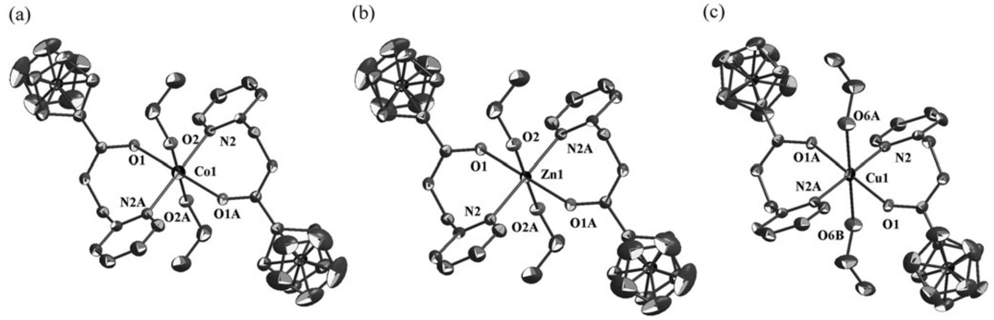

Figure 1. Perspective figures of the structures of **1** (a), **2** (b), and **3** (c), showing 30% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

Table 3. Hydrogen-bond geometry (Å, °) for **1–3**.

	D–H···A	D–H	H···A	D···A	DHA
1	N1–H1···O5	0.860	2.260	3.076	158.39
	O2–H2···O3^{i}	0.850	2.060	2.847	153.59
2	N1–H1···O3	0.900	2.631	3.056	109.80
	O2–H2···O4^{i}	0.850	2.026	2.848	162.56
3	N1–H1···O4^{ii}	0.900	2.618	3.237	126.68
	O6–H6···O2^{iii}	0.820	2.254	3.028	157.49

Note: Symmetry codes: i, x, y, $z-1$; ii, $-x$, $y-1/2$, $-z+1/2$ and iii, x, $-y+3/2$, $z+1/2$.

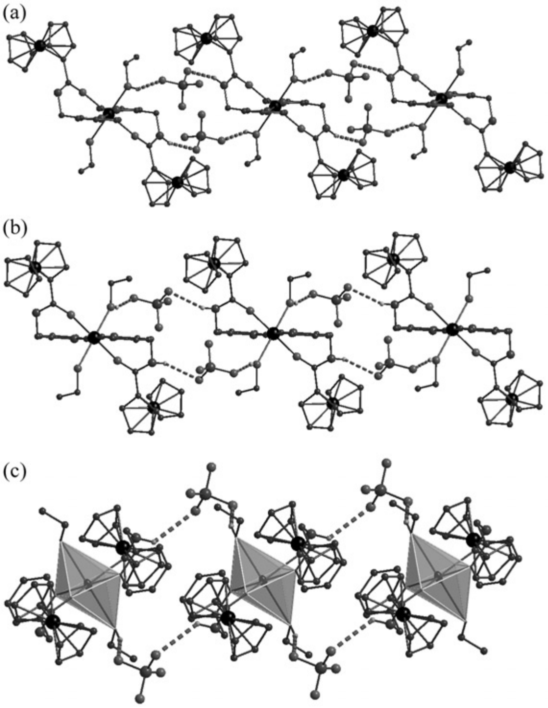

Figure 2. Molecular packing diagrams showing intermolecular H-bonding between M(II) complex and perchlorates [M = Co (a), Zn (b), and Cu (c)].

ethanol from two neighboring complex cations. The O ⋯ O and O ⋯ N distances are 2.847 and 3.076 Å for **1**, 2.848 and 3.056 Å for **2**, and 3.028 and 3.237 for **3**, respectively. Thus, the adjacent $[M(2\text{-PAMF})_2(CH_3CH_2OH)_2]$ (M = Co **1**, Zn **2**, and Cu **3**) cations are linked by ClO_4^- ions via hydrogen bonds to build an infinite supramolecular chain (figure 2).

Coordination of the metal complexes by the three donor atoms on 2-PAMF ligand was modulated by the use of base and the steric effect of the substituents. When neutral, the amide on 2-PAMF is protonated and the pyridyl N and O from the amide chelating the metal as a bidentate ligand. The bulky ferrocene introduces strong steric hindrance, with 2-PAMF in the three compounds chelating in a seven-membered ring, not a five-membered ring (figure 3). Further reactions of 2-PAMF and metal salts under basic conditions are the subject of ongoing study.

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) (Email: deposit@ccdc.cam.ac.uk) as supplementary materials and the CCDC reference numbers for **1**, **2**, and **3** are 690746, 690745, and 690744, respectively.

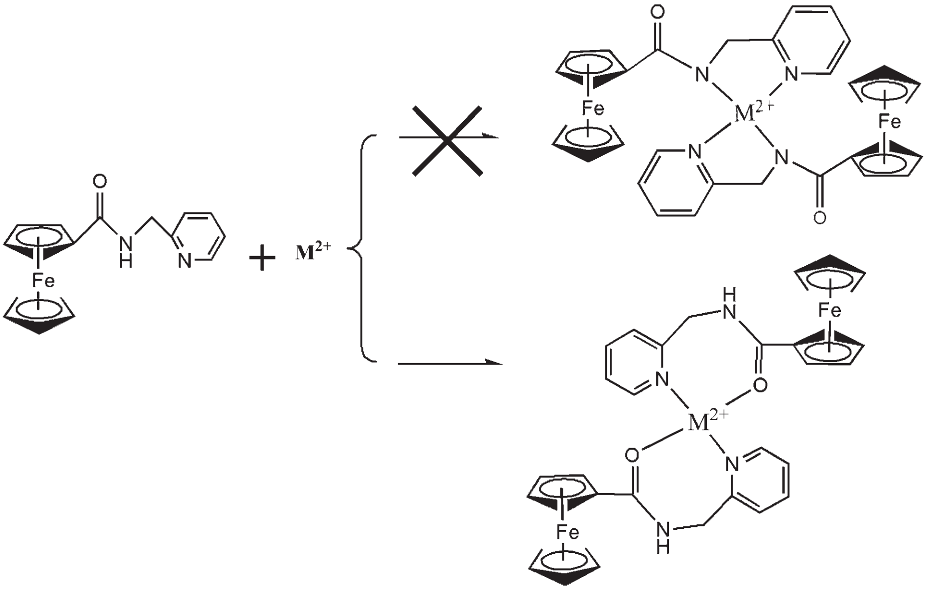

Figure 3. The seven-membered chelation ring formed by complexation.

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