First examples of homo-/heteroleptic bi-/tri-nuclear complexes containing 5-ferrocenyldipyrromethene†

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The first examples of homo- and heteroleptic complexes containing 5-ferrocenyldipyrromethene (fcdpm) [Cu(fcdpm)$_2$] (**1**) [Cu(fcdpm)(acac)] (**2**), [Ni(fcdpm)(acac)] (**3**) and [Zn(fcdpm)$_2$] (**4**) (acac = acetylacetonato) are described. Formation of the asymmetric metal complexes has been followed by electronic absorption and infrared spectroscopy. The complexes have been characterised by elemental analyses and spectral studies. Structures of [Cu(fcdpm)$_2$] (**1**), [Cu(fcdpm)(acac)] (**2**) and [Ni(fcdpm)(acac)] (**3**) have been determined crystallographically. Structural data revealed that the metal centre in the copper complexes [Cu(fcdpm)$_2$] (**1**), [Cu(fcdpm)(acac)] (**2**) and the nickel complex [Ni(fcdpm)(acac)] (**3**) adopts a distorted square planar geometry.

Introduction

Immense current interest has arisen in the chemistry of transition metal complexes containing a redox active ferrocene moiety owing to their potential applications in catalysis,[1] designing of new non-linear optical materials,[2] biologically active compounds,[3] and as anticancer agents.[4] In this context efforts are being made to develop systems that allow interactions between the ferrocene iron and additional metal ions bound at the side chains of the cyclopentadienyl rings.[5] Further, *meso*-substituted dipyrrins and their compounds have drawn considerable current attention owing to their rich optical properties.[6] Synthesis of the *meso*-substituted dipyrrins can be easily achieved by condensation of respective aldehydes with pyrrole followed by oxidation.[7] One can fine tune the properties of the dipyrrins by introducing electron withdrawing/donating substituents, which strongly influence their electrochemical and optical properties.[8] An extensive π-skeleton of the substituted phenyl ring as the *meso*-substituent and two conjugated rigid pyrrole rings present in the dipyrrins enable them to behave as better bidentate nitrogen donors than ligands such as 2,2′-bipyridine or 1,10-phenanthroline.

The combination of a dipyrrin and organometallic fragments within the same molecule may be interesting in terms of both the catalytic properties and intramolecular charge transfers.[1,2] 5-Ferrocenyldipyrromethane having a ferrocenyl group as the *meso*-substituent was reported by Moriarty *et. al*, in 1999.[9] A literature survey revealed that despite detailed reports concerning complexes of porphyrins based on 5-ferrocenyldipyrromethene, the reactivity of this interesting ligand has not been examined with transition metal ions/complexes.[9] In view of the potential synthetic importance of the transition metal complexes based on dipyrrin ligands and of our continuing interest in this area, we have started a systematic study on the reactivity of fcdpm with transition metal/ions complexes.[10] In this paper we report reproducible synthesis and characterisation of homo- and heteroleptic dipyrrinato metal complexes [Cu(fcdpm)$_2$], [Cu(fcdpm)(acac)], [Ni(fcdpm)(acac)] and [Zn(fcdpm)$_2$] (acac = acetylacetonato) Also, we present herein the crystal structures of the complexes [Cu(fcdpm)$_2$] (**1**), [Cu(fcdpm)(acac)] (**2**) and [Ni(fcdpm)(acac)] (**3**).

Experimental

All the reagents and solvents were purchased from commercial sources and used as received. NMR spectra were recorded in $CDCl_3$ solution with a JEOL AL 300 FT-NMR machine at an operating frequency of 300 MHz. Chemical shifts (δ) are given in ppm relative to TMS. Elemental analyses (C, H and N) were performed on a CE-440 CHN analyser. IR and UV/Vis spectra were obtained on Perkin-Elmer 577 and Shimadzu UV-1601 spectrophotometers, respectively. 5-Ferrocenyldipyrromethane was prepared and purified following the literature procedures.[9]

Preparation of the complexes

Synthesis of [Cu(fcdpm)$_2$] (1). 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (0.31 g, 1.34 mmol) dissolved in 100 mL of benzene was added dropwise under stirring to a solution of 5-ferrocenyldipyrromethane (0.438 g, 1.34 mmol) in 150 mL of $CHCl_3$ cooled in an ice bath. After the addition was complete, the solvent was evaporated to half its volume under reduced pressure and $CuCl_2{\cdot}2H_2O$ (0.092 g, 0.54 mmol) dissolved in 50 mL of MeOH was introduced to the reduced solution. The reaction mixture was stirred for 2 hours to form the copper complex. The resulting solution was evaporated to dryness and the product was purified by column chromatography (SiO_2; $CHCl_3$ with 10% hexane) to afford a dichroic blue/green solid. Yield: 0.287 g (40%). Anal. Calcd for $C_{38}H_{30}N_4Fe_2Cu$: C, 63.59; H, 4.22; N, 7.81%. Found: C, 63.30; H, 4.27; N, 7.74%. UV-Vis. (CH_2Cl_2, λ_{max} nm, ε M^{-1} cm^{-1}): 483 (3.36×10^4) 348 (2.02×10^4), 236 (2.08×10^4).

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IR (KBr pellets, cm^{-1}): 428, 500, 602, 655, 731, 771, 828, 885, 993, 1043, 1205, 1242, 1330, 1376, 1402, 1441, 1523, 1588, 2922, 3092.

[Cu(fcdpm)(acac)] (2). This complex was prepared following the above procedure except that Cu(acac)$_2$ was used in place of $CuCl_2 \cdot 2H_2O$. The resulting solution was evaporated to dryness and product was purified by column chromatography (SiO_2; $CHCl_3$ with 10% hexane) to afford blue/green crystals. Yield: 0.220 g (45%). Anal. Calcd for $C_{24}H_{22}N_2O_2FeCu$: C, 58.89; H, 4.53; N, 5.72. Found: C, 59.18; H, 4.61; N, 5.63. UV-Vis. (CH_2Cl_2, λ_{max} nm, ε M^{-1}cm^{-1}): 503 (3.31×10^4) 344 (1.70×10^4), 299 (1.82×10^4), 238 (2.42×10^4). IR (KBr pellets, cm^{-1}): 492, 600, 656, 729, 770, 810, 884, 993, 1034, 1102, 1204, 1238, 1329, 1393, 1527, 1588, 2912, 3091.

[Ni(fcdpm)(acac)] (3). The same procedure was used as in the synthesis of [Cu(fcdpm)$_2$] except that [Ni(acac)$_2$] was used in place of [Cu(acac)$_2$]. Yield: 0.232 g (48%). Anal. Calcd for $C_{24}H_{22}N_2O_2FeNi$: C, 59.50; H, 4.58; N, 5.79. Found: C, 59.78; H, 4.68; N, 5.86. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.93 (s, 6H), 4.19 (s, 5H), 4.46 (s, 2H), 4.73 (s, 2H), 5.49 (s, 1H), 6.27 (q, 4H, J = 2.4 Hz), 7.58 (q, 2H, J = 3.6 Hz). UV-Vis. (CH_2Cl_2, λ_{max} nm, ε M^{-1} cm^{-1}): 514 (2.33×10^4) 435 (1.16×10^4), 344 (2.00×10^4), 240 (3.81×10^4). IR (KBr pellets, cm^{-1}): 485, 595, 658, 727, 766, 818, 889, 1001, 1034, 1103, 1206, 1243, 1341, 1382, 1531, 1575, 2922, 3093.

[Zn(fcdpm)$_2$] (4). This complex was synthesized following the method for [Cu(fcdpm)$_2$] using [Zn(acetate)$_2$] in place of $CuCl_2 \cdot 2H_2O$. Yield: 0.302 g (42%). Anal. Calcd for $C_{24}H_{22}N_2O_2FeZn$: C, 63.41; H, 4.20; N, 7.78. Found: C, 63.70; H, 4.26; N, 7.70. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 4.20 (s, 10H), 4.56 (s, 4H), 4.84(s, 4H), 6.43 (q, 8H, J = 3.0 Hz), 7.94 (d, 4H, J = 2.4 Hz). UV-Vis. (CH_2Cl_2, λ_{max} nm, ε M^{-1}cm^{-1}): 494 (3.30×10^4) 347 (1.53×10^4), 239 (2.07×10^4). IR (KBr pellets, cm^{-1}): 486, 595, 668, 732, 772, 828, 887, 989, 1037, 1171, 1208, 1236, 1331, 1374, 1401, 1515, 1588, 2927.

X-ray crystallography

Suitable crystals of **1**, **2** and **3** for single-crystal X-ray diffraction analyses were obtained from a mixture of dichloromethane and hexane at room temperature. Preliminary data on the space group and unit cell dimensions as well as intensity data were collected on an OXFORD DIFFRACTION X CALBER-S diffractometer using graphite monochromated Mo-K_α radiation. Structures were solved by direct methods and refined using SHELX-97.[11] The non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were geometrically fixed and refined using a riding model. The computer program PLATON was used for analyzing the interaction and stacking distances.[12]

Results and discussion

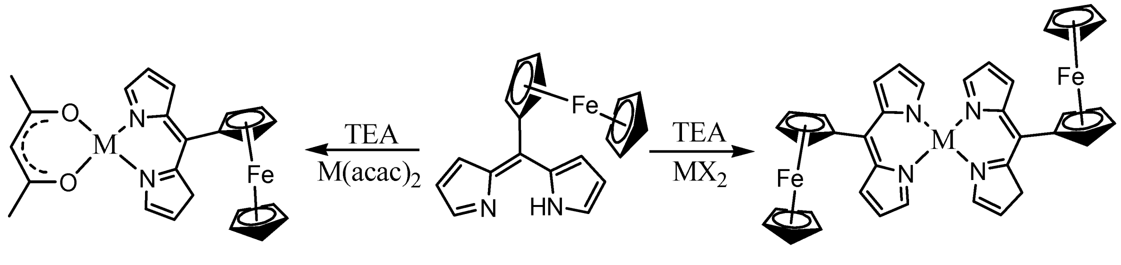
Synthesis and structural studies

The homoleptic dipyrrinato metal complexes [M(fcdpm)$_2$] (M = Cu, Zn) were synthesised by the treatment of respective metal salts to a solution containing 5-ferrocenyldipyrromethene obtained *in-situ* by oxidation of 5-ferrocenyldipyrromethane with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in a mixture of CH_2Cl_2/CH_3OH (1:1, v/v) at room temperature. A simple scheme showing the syntheses of the complexes is depicted in Scheme 1. The heteroleptic complexes [M(fcdpm)(acac)] (M = Cu, Ni) were prepared in an analogous manner by the reaction of M(acac)$_2$ (M = Cu, Ni) with 1 equiv of oxidized dipyrromethane in CH_2Cl_2/CH_3OH (1:1, v/v).

Following the extractive workup and recrystallizations from dichloromethane/hexane mixtures pure complexes were obtained in moderate yields (~ 40–48%). The complexes **1**–**4** are air-stable, highly soluble in common organic solvents like dichloromethane, chloroform, acetone, dimethyl sulfoxide, acetonitrile, ethanol, methanol, and sparingly soluble in diethyl ether, petroleum ether and hexane.

The complexes were fully characterised by IR, UV-Vis and EPR spectroscopic studies. All the complexes gave satisfactory analyses for C, H and N (recorded in the Experimental section). Infra-red spectra of the respective complexes displayed diagnostic bands associated with the coordinated fcdpm and acac ligands.[13] In its absorption spectra, heteroleptic complexes [Cu(fcdpm)(acac)] and [Ni(fcdpm)(acac)] displayed absorption bands around 344/344 and 503/514 nm, while homoleptic complexes [Cu(fcdpm)$_2$] and [Zn(fcdpm)$_2$] exhibited major transitions at 348/347 and 483/494 nm (Fig. 1). Intense low-energy transitions in the absorption spectra of the respective complexes (503/514/483/494 nm) have been assigned to the charge-transfer processes associated with the dipyrrin ligand.[14–16] The intense bands in the UV region 238–347 nm have been assigned to the ligand centered intra-ligand transitions.

The ^{1}H-NMR-spectroscopic investigations on **3** revealed that the ferrocenyl groups in this complex are unsymmetrical. Cyclopentadienyl ring protons of the free ligand splits and gives three distinct signals upon coordination to the metal centre. The ^{1}NMR spectrum **3** displayed resonances at 1.93 {(s, 6H, acac (Me)}, 4.19



M = Cu^{2+} (**2**), Ni^{2+} (**3**)

M = Cu^{2+} (**1**), Zn^{2+} (**4**)

Scheme 1

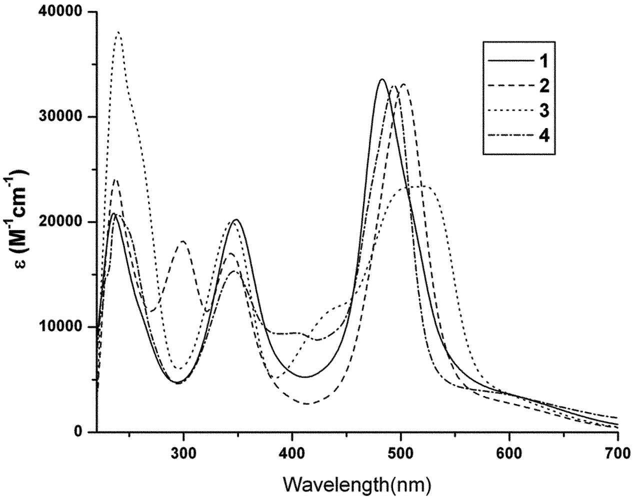


Fig. 1 UV-visible absorption spectra of the complexes **1–4**.

(s, 5H, Cp), 4.46 (s, 2H, Cp), 4.73 (s, 2H, Cp), 5.49 {(s, 1H, acac (CH)}, 6.24 (q, 4H, J = 2.4 Hz, H-*pyr*), 7.58 (q, 2H, J = 3.6 Hz, H-*pyr*) ppm. This observation of ^{1}H NMR can be interpreted in terms of the geometry of the complex. Despite a slight distortion from the square-planar environment of the nickel(II) centre, complex **3** is found to be in a low-spin state and therefore, is diamagnetic in nature. This finding is further supported by the results obtained from X-ray diffraction studies on complex **3**. An analogous pattern of the resonances has been observed for complex **4** also. It displayed slightly deshielded resonances at 4.20 (s, 10H, Cp), 4.56 (s, 4H, Cp), 4.84(s, 4H, Cp), 6.43 (q, 8H, J = 3.0 Hz, H-*pyr*), 7.94 (d, 4H, J = 2.4 Hz, H-*pyr*) corresponding to coordinated fcdpm ligands.

Information about the immediate environment of the metal centres in complexes **1** and **2** has also been derived from ESR spectral studies. The X-band ESR spectra of **1** and **2** in DCM were recorded both at liquid-nitrogen and room temperatures (Figure S1-2†). Spectra of both complexes **1** and **2** displayed four well resolved peaks at room temperature, while in the frozen state they exhibited one and three peaks, respectively. The copper complex **1** exhibited $g_{\parallel}$ value of 2.2206, $g_{\perp} = 2.023$ and $g_{\text{iso}} = 2.145$, while these values for complex **2** were found to be 2.197, 2.032 and 2.087, respectively. The greater $g_{\parallel}$ values indicate larger twisting of the ligand planes in the homoleptic complex **1** (ω~46°) as compared to that of the square-planar heteroleptic complex **2** (ω~2.6), which may be ascribed to the lower steric congestion.[17–18]

Crystal structures of the homoleptic complex **1** and heteroleptic complexes **2** and **3** have been determined crystallographically. Details about the data collection, structure solution and refinement are listed in Table 1. Crystal structures of the complexes **1**, **2** and **3** with atomic numbering scheme is shown in Fig. 2 (a,b,c) and important geometrical parameters are collected in Table 2. The crystal structure of complex **1** revealed that the coordination geometry about the metal centre copper is completed by nitrogen atoms N1, N2, N3 and N4 of the coordinated dipyrrins in a bis-chelating mode. It adopted a highly distorted square planar geometry, a feature typical of bis-(dipyrrin) metal complexes.[15–16] The inability of these compounds to form more idealized square planar complexes may be attributed to a steric clash between the α-pyrrolic protons on the opposing ligands (the angle between the CuN1N2 and CuN3N4 planes, is 46.25°).[13,16]

The Cu–N (pyrrole) bond distances Cu(1)–N(1), Cu(1)–N(2), Cu(1)–N(3) and Cu(1)–N(4) in this complex are 1.962(6) 1.952(7) 1.967(7) and 1.946(6), respectively. The *trans* Cu(1)–N(1), Cu–N(3) bond distances are almost equal and comparable to the Cu–N distances reported in the literature.[13] The N(1)–Cu–N(2) and N(1)–Cu–N(3) angles are 91.4(3)°, 148.3(3)° respectively, which shows a large distortion from the square planar geometry. The ferrocenyl groups are twisted perpendicular to the dipyrrin

Table 1 Crystal data and structure refinement parameters for **1**, **2** and **3**

	1	**2**	**3**
Empirical formula	$C_{38}H_{30}N_4Fe_2Cu$	$C_{48}H_{44}N_4O_4Cu_2Fe_2$	$C_{24}H_{22}N_2O_2Fe_2Ni$
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*	*P*2$_1$/*c*
a (Å)	31.485(4)	22.903(5)	16.3441(9)
b (Å)	8.1551(10)	15.047(5)	11.8082(8)
c (Å)	23.249(4)	13.607(5)	10.6964(7)
α (deg)	90.00	90.000(5)	90.00
β (deg)	106.384(18)	123.984(5)	101.557(6)
γ (deg)	90.00	90.000(5)	90.00
V (Å^3), *Z*	5727.0(14), 8	3888(2), 4	2022.5(2), 4
λ (Å)	0.71073	0.71073	0.71073
Color and habit	Black, Block	Black, Block	Black, Block
T (K)	150(2)	150(2)	150(2)
Reflns collected	5054	3426	3538
Reflns/restraint/params	3520/0/406	3426/0/273	3538/0/273
D_{calcd} (Mg m^{-3})	1.665	1.673	1.593
μ (mm^{-1})	1.773	1.865	1.672
GOF on F^2	1.073	0.926	1.149
Final *R* indices $I>2\sigma(I)^a$	$R1 = 0.0886$ $wR2 = 0.2311$	$R1 = 0.0454$ $wR2 = 0.1142$	$R1 = 0.0625$ $wR2 = 0.1830$
R indices (all data)^a	$R1 = 0.1200$ $wR2 = 0.2988$	$R1 = 0.0597$ $wR2 = 0.1177$	$R1 = 0.0901$ $wR2 = 0.2507$

^{a} $R_1 = \sum||F_o| - F_c||/\sum|F_o|$; $R_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[wF_o^4]\}^{1/2}$.

Table 2 Selected bond lengths (Å) and angles (deg) for **1**, **2** and **3**

1		**2**		**3**	
Cu1–N1	1.962(6)	Cu1–N1	1.940(7)	Ni1–N1	1.884(6)
Cu1–N2	1.952(7)	Cu1–N2	1.959(7)	Ni1–N2	1.895(6)
Cu1–N3	1.967(7)	Cu1–O1	1.935(7)	Ni1–O1	1.881(5)
Cu1–N4	1.946(6)	Cu1–O2	1.931(6)	Ni1–O2	1.855(5)
C5–C19	1.511(10)	C10–C15	1.485(12)	C10–C15	1.478(10)
C14–C29	1.499(10)				
N2–Cu1–N1	91.4(3)	N1–Cu1–N2	89.9(3)	N1– Ni1–N2	91.2(3)
N1–Cu1–N3	148.3(3)	O2–Cu1–O1	91.1(3)	O2– Ni1–O1	93.0(2)
N4–Cu1–N3	90.2(3)	O1–Cu1–N1	88.3(3)	O1– Ni1–N1	88.3(3)
N4–Cu1–N2	146.5(3)	O2–Cu1–N1	177.6(3)	O2– Ni1–N1	172.7(2)
C4–C5–C19–C20	−39.4(10)	O1–Cu1–N2	177.8(3)	O1– Ni1–N2	173.4(2)
C15–C14–C29–C33	34.3(12)	O2–Cu1–N2	90.7(3)	O2–Ni1–N2	88.3(2)
		C11–C10–C15–C19	37.5(14)	C9–C10–C15–C19	39.4(10)
Cu···Cu (shortest)	5.945	Cu···Cu (shortest)	4.189	Ni···Ni (shortest)	6.437
ω^a	46.25	ω^b	2.64	ω^c	9.61

[a] Angle between CuN1N2 and CuN3N4 planes. [b] Angle between CuO2 and CuN2 planes. [c] Angle between NiO1O2 and NiN1N2 planes.

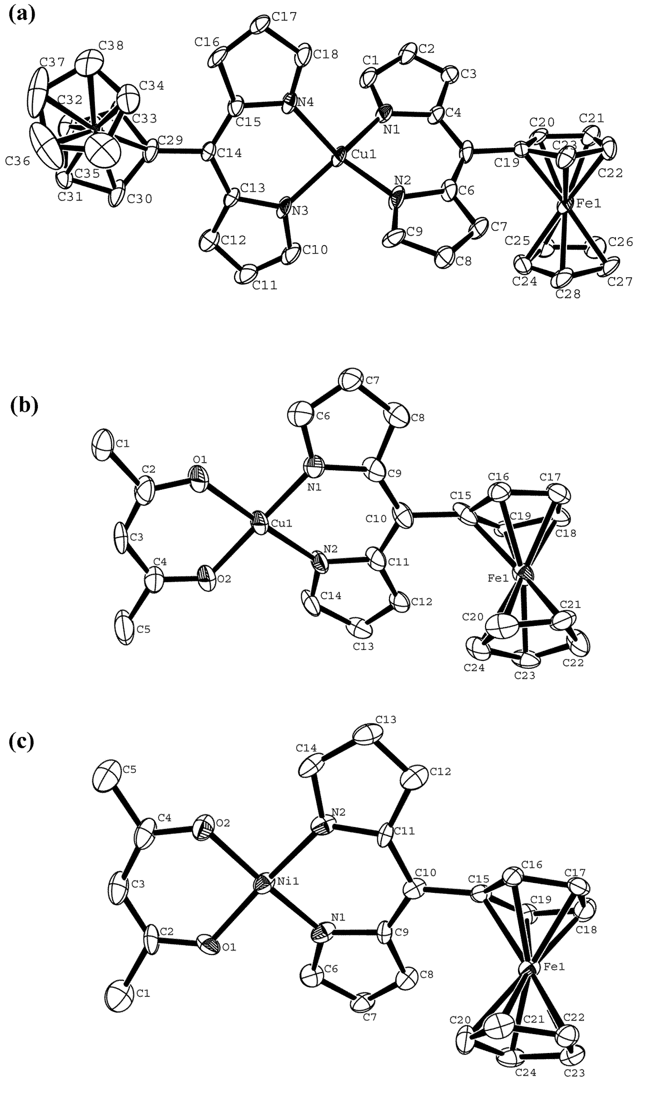


Fig. 2 Crystal structures of complexes **1** (a), **2** (b), and **3** (c) at 30% thermal ellipsoid probability (hydrogen atoms omitted for clarity).

plane with dihedral angles of (C4 C5 C19 C20, C15 C14 C29 C33) of –39.4(10)°, 34.3(12)°.

The asymmetric unit of **2** contains one copper atom bonded with two pyrrole nitrogen atoms of the dipyrromethene unit and two oxygen atoms of the acac resulting in a square planar geometry. In this case, Cu(1)–N(1) and Cu(1)–O(1) bond lengths are 1.940(7) and 1.935(7) Å, respectively which are similar to those observed in other dipyrrin [Cu(dpm)(acac)] complexes (Table 2).[19–21] The Cu(1)–N(1) (dipyrrin) distances are somewhat shorter than the Cu–N distance in the homoleptic complex **1** and shows that the dipyrrin unit is strongly bonded to the metal centre copper. The angles N(1)–Cu(1)–N(2), O(2)–Cu(1)–O(1), O(2)–Cu(1)–N(1) and O(2)–Cu(1)–N(1) are 89.9(3)°, 91.1(3)°, 88.3(3)°, 177.6(3)°, respectively. It suggested square-planar geometry about the metal centre. The ferrocenyl group is twisted with respect to the dipyrrin plane by 37.5(14)°. The molecular structure of complex **3** is analogous to that of **2**. The Ni1–N1, Ni1–N2, Ni1–O2 and Ni1–O1 bond distances are 1.884(6), 1.895(6), 1.855(5) and 1.881(5), respectively. The bond angles, between NiN_2 and NiO_2 planes show that the distortion from the square-planar arrangement of various groups in this complex is greater than that in

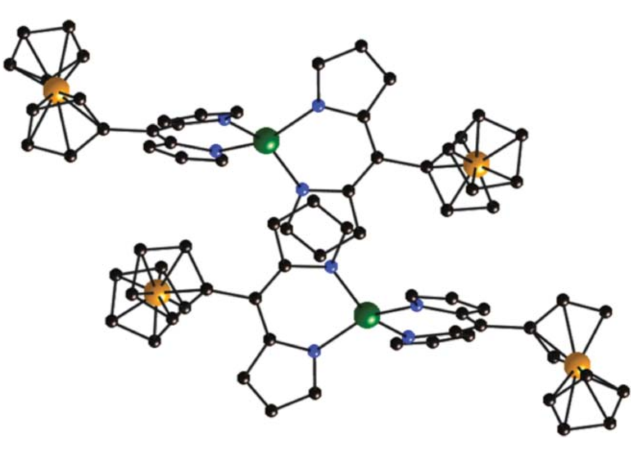


Fig. 3 Pseudo-dinuclear system resulting from π···π stacking interactions in complex **1**.

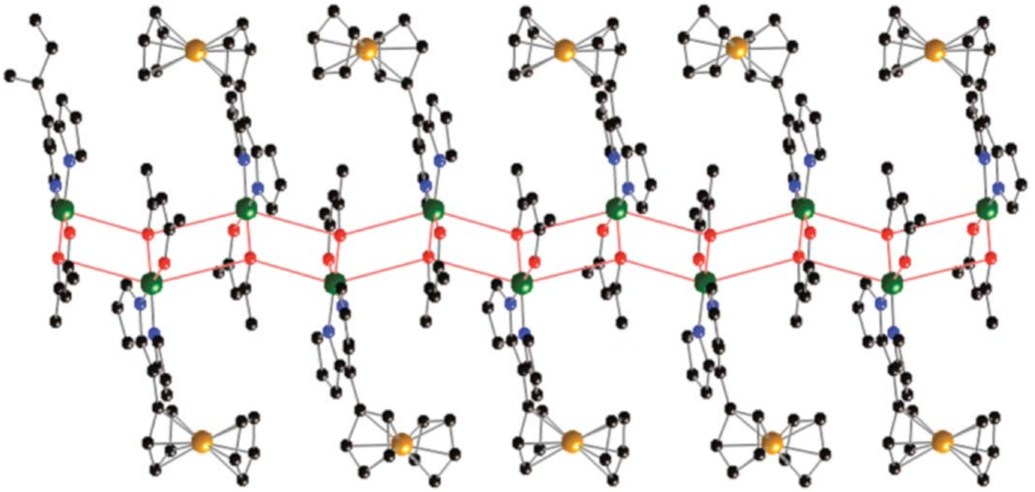


Fig. 4 Pseudo-one-dimensional system with Cu–Cu (4.45 Å) and Cu–O (3.7 Å) distances in complex **2**.

complex **2**. A notable structural feature of complex **3** is that in this case the ferrocenyl cyclopentadienyl rings are almost eclipsed (angle 1.79°), while in Cu complexes (**1** and **2**) the cyclopentadienyl rings are displaced by 12.27° and 12.71°, respectively.

Matrices for weak hydrogen bonding interactions in these complexes are presented in Table S1.† Weak interaction studies on complex **1** revealed the presence of C–H···π [H···Cg distances are 2.68, 2.93, 2.81 Å] and π–π stacking interactions [(π–π distance = 3.447 Å] (Fig. 3). In this complex although Cu···Cu contacts are longer (5.945 Å), the π–π stacking interaction results in the formation of a pseudo-dinuclear system.[18] The crystal packing in **2** is also stabilized by C–H···π interactions [H···Cg distances 2.78, 2.81, 2.99, 2.84 Å], which leads to a linear structural motif as shown in Fig. 4. Further, the crystal structure of complex **2** displayed a stacked arrangement along the crystallographic '*a*'-axis with Cu···Cu separations of 4.455 and 4.189 Å (Table 2). The interesting feature of complex **3** is that in this complex a rectangular grid-like motif is formed *via* the C–H···π interactions [H···Cg distances are 2.70, 2.63, 2.96 Å] along the crystallographic '*a*'-axis (Figure S3†). The distances of weak bonding interactions are comparable to the values reported in the literature.[22]

Conclusions

Through this work an attempt has been made to synthesise and characterise homo- and heteroleptic complexes based on 5-ferrocenyldipyrromethene for the first time. Four new complexes containing 5-ferrocenyldipyrromethene (fcdpm) with the formulations [Cu(fcdpm)$_2$], [Zn(fcdpm)$_2$], [Cu(fcdpm)(acac)] and [Ni(fcdpm)(acac)] have been synthesised and characterised by analytical and spectral studies. Molecular structures of the copper complexes [Cu(fcdpm)$_2$] and [Cu(fcdpm)(acac)], and nickel complex [Ni(fcdpm)(acac)] (**3**) have been authenticated crystallographically.

Acknowledgements

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