

Synthesis and characterization of some heteroleptic copper(II) complexes based on *meso*-substituted dipyrrens

RAKESH KUMAR GUPTA, MAHENDRA YADAV, RAMPAL PANDEY and
DAYA SHANKAR PANDEY*

Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi 221005, India
e-mail: dspbhu@bhu.ac.in

Abstract. The syntheses and characterizations of *meso*-substituted dipyrrens, 5-(4-imidazol-1-yl-phenyl)-dipyromethene (4-impdpm), 5-(4-nitro-imidazol-1-yl-phenyl)-dipyromethene, (4-nimpdpm), 5-(4-benzimidazol-1-yl-phenyl)-dipyromethene (4-bimpdpm) and heteroleptic complexes $[\text{Cu}_3(4\text{-impdpm})_2(\text{hfacac})_4]$ **1**, $[\text{Cu}(4\text{-nimpdpm})(\text{acac})]$ **2**, $[\text{Cu}(4\text{-nimpdpm})(\text{hfacac})]$ **3**, $[\{\text{Cu}(4\text{-bimpdpm})(\text{acac})\}_n]$ **4** and $[\{\text{Cu}(4\text{-bimpdpm})(\text{hfacac})\}_n]$ **5**, imparting acetylacetonato (acac) and hexafluoroacetylacetonato (hfacac) groups as co-ligand have been described. The dipyrrens and complexes **1–5** have been characterized by elemental analyses and spectral (IR ESI-MS, NMR, electronic absorption and emission) studies. Crystal structures of **1**, **3** and **4** have been authenticated by X-ray single crystal analyses. The reaction between 4-impdpm and $\text{Cu}(\text{hfacac})_2$ gave a trimetallic complex, under analogous conditions 4-nimpdpm and 4-bimpdpm reacted with $\text{Cu}(\text{acac})_2$ and $\text{Cu}(\text{hfacac})_2 \cdot 2\text{H}_2\text{O}$ to afford mononuclear (**2**, **3**) and 1D polymeric (**4**, **5**) complexes.

Keywords. Coordination polymers; *meso*-substituted dipyrrens; heteroleptic; acetylacetonato; hexafluoroacetylacetonato; copper complexes.

1. Introduction

The chemistry of coordination polymers has seen a large surge during past couple of decades because of their intriguing architectures, topologies, and potential application in diverse areas.^{1–9} With an objective of developing functional materials possessing desirable properties numerous systems have been synthesized through the judicious choice of ligands and metal ions.^{10–15} The creation of coordination polymers largely depend on geometry of the metal ions, nature of the ligand, metal to ligand ratio, solvent systems, counter anions and the pH of reaction medium.^{16–19} Among these, the choice of ligand plays crucial role in the formation of coordination polymers. In addition, the design and synthesis of dipyrromethenes (dipyrrens) has been attractive because of their rather easy synthesis and functionalization as well as monoanionic and chelating nature of their conjugate base and extensive use in various areas.^{20–28} A large number of charge neutral homo-/heteroleptic complexes and supramolecular clusters imparting dipyrrens has been synthesized and thoroughly studied.^{20,21} It has been established that suitably designed *meso*-substituted dipyrrens find wide applications in the synthesis of extended homo-/heterometallic architectures.^{20–22}

Further, imidazolyl-dipyrrens are of particular interest in materials chemistry and life sciences.^{29–31} With an objective of developing extended architectures based on *meso*-substituted dipyrrens and to examine the role of *meso*-substituent on ensuing complexes, 4-impdpm, 4-nimpdpm and 4-bimpdpm have been synthesized and their reactivity examined with Cu(II) complexes $\text{Cu}(\text{acac})_2$ and $\text{Cu}(\text{hfacac})_2 \cdot 2\text{H}_2\text{O}$. Through this contribution we present the synthesis and characterization of *meso*-substituted dipyrrens and Cu(II) complexes $[\text{Cu}_3(4\text{-impdpm})_2(\text{hfacac})_4]$ **1**, $[\text{Cu}(4\text{-nimpdpm})(\text{acac})]$ **2**, $[\text{Cu}(4\text{-nimpdpm})(\text{hfacac})]$ **3**, $[\{\text{Cu}(4\text{-bimpdpm})(\text{acac})\}_n]$ **4**, and $[\{\text{Cu}(4\text{-bimpdpm})(\text{hfacac})\}_n]$ **5**. Also, we present here X-ray single crystal structures of **1**, **3** and **4**.

2. Experimental

The solvents were rigorously purified by standard procedures prior to their use.³² Imidazole, 4-nitroimidazole, benzimidazole, 4-fluorobenzaldehyde, trifluoroacetic acid (TFA), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), triethylamine, $\text{Cu}(\text{hfacac})_2 \cdot 2\text{H}_2\text{O}$ and silica gel (200–400 mesh) were procured from Sigma Aldrich Chemical Co., USA and used as received without further purifications. The ligands

*For correspondence

4-impdpm, 4-nimpdpm and 4-bimpdpm were synthesized by the procedure described by Magdolen *et al.* with slight modifications³³ and the precursor complex Cu(acac)₂ following literature procedure.³⁴ Elemental analyses for C, H and N were performed on an Exeter Analytical Inc. Model CE-440 Elemental Analyzer. IR spectra (4000–400 cm⁻¹) were acquired on a Varian 3300 FT-IR spectrometer. Electronic absorption and emission spectra were obtained on Shimadzu UV-1701 and Varian Cary Eclipse Fluorescence spectro-photometers, respectively. ¹H (300 MHz) NMR spectra was acquired on a JEOL AL300 FT-NMR spectrometer using tetramethylsilane (TMS) as an internal reference. Room temperature magnetic susceptibility measurements were performed on a Cahn–Faraday balance using Hg[Co(SCN)₄] as a calibrant.

2.1 Syntheses

2.1a 5-(4-imidazol-1-yl-phenyl)-dipyrromethane (4-impdpm): To a flask containing pyrrole (19.34 g), 4-imidazol-1-yl-benzaldehyde (3.44 g, 0.02 mol) was added and heated at 120°C with stirring under inert atmosphere for 24 h. After cooling to ambient temperature it was concentrated to dryness under reduced pressure and the crude product purified by column chromatography [alumina; ethylacetate: dichloromethane (1 : 1)]. Yield: 38% (2.19 g). *Anal.* Calc. for C₁₈H₁₆N₄: C, 74.96; H, 5.60; N, 19.44%. Found: C, 75.29; H, 5.47; N, 19.52%. ¹H NMR (CDCl₃, δ ppm): 5.54 (s, 1H, *meso*-H), 5.92 (s, 2H, pyr-H), 6.18 (q, 2H, *J* = 3.0 Hz, pyr-H), 6.74 (s, 2H, pyr-H), 7.19–7.32 (m, 6H), 7.80 (s, 1H, imi-H), 8.04 (bs, 2H, NH). IR (KBr pellet, cm⁻¹): 3255, 3115, 2966, 1655, 1567, 1518, 1431, 1305, 1253, 1112, 1058, 819, 774, 724.

2.1b 5-(4-(4-nitro-imidazol)-1-yl-phenyl)-dipyrromethane (4-nimpdpm): It was prepared by following the above procedure for 4-impdpm using 4-(4-nitro-imidazol-1-yl)-benzaldehyde (4.34 g, 0.02 mol). Yield: 40% (2.67 g). *Anal.* Calc. for C₁₈H₁₅N₅O₂: C, 64.84; H, 4.54; N, 21.01%. Found: C, 65.00; H, 4.62; N, 21.30%. ¹H NMR (CDCl₃, δ ppm): 5.46 (s, 1H, *meso*-H), 5.89 (s, 2H, pyr-H), 6.18 (s, 2H, pyr-H), 6.70 (s, 2H, pyr-H), 7.35–7.40 (m, 4H), 7.71 (s, 1H, imi-H), 8.04 (bs, 2H, NH), 8.06 (s, 1H, imi-H). IR (KBr pellet, cm⁻¹): 3248, 3124, 2968, 1678, 1610, 1590, 1542, 1514, 1490, 1426, 1406, 1350, 1304, 1268, 1122, 1092, 1068, 1024, 822, 774, 732.

2.1c 5-(4-benzimidazol-1-yl-phenyl)-dipyrromethane (4-bimpdpm): It was prepared by following the above procedure for **1** using 4-impdpm (4.44 g, 0.02 mol). Yield: 50% (3.85 g). *Anal.* Calc. for C₂₂H₁₈N₄: C, 78.08; H, 5.36; N, 16.56%. Found: C, 78.15; H, 5.39; N, 16.49%. ¹H NMR (CDCl₃, δ ppm): 5.59 (s, 1H, *meso*-H), 5.60 (s, 2H, pyr-H), 6.18 (s, 2H, pyr-H), 6.77 (s, 2H, pyr-H), 7.35–7.40 (m, 6H), 7.56 (s, 1H), 7.79 (s, 1H), 7.82 (s, 1H, imi-H), 8.58 (bs, 2H, NH), IR (KBr pellet, cm⁻¹): 3256, 3122, 2961, 1676, 1615, 1581, 1543, 1517, 1492, 1423, 1408, 1350, 1305, 1265, 1120, 1095, 1068, 1025, 823, 773, 730.

2.1d [Cu₃(4-impdpm)₂(hfacac)₄] (1): To a stirring ice cooled dichloromethane solution (50 mL) of 4-impdpm (0.288 g, 0.001 mol), DDQ (0.228 g, 1.0 mmol) dissolved in benzene (30 mL) was added drop-wise and stirred for an hour. A methanolic (20 mL) solution of Cu(hfacac)₂·2H₂O (0.496 g, 0.001 mol) was added to it and stirred for 20 min. The reaction mixture was evaporated to dryness and crude product purified by column chromatography (SiO₂: CHCl₃ with 1% MeOH) to afford a red solid. Dichroic reddish-green crystals of **1** were obtained from CH₂Cl₂/ hexane (1 : 1) solution. Yield: 30% (0.190 g). *Anal.* Calc. for C₃₆H₂₆N₈Cu: C, 68.18; H, 4.13; N, 17.67%. Found: C, 68.38; H, 4.30; N, 17.55%. ESI-MS (*m/z*) obs (calcd.): 634 [M+H]⁺ (634). IR (KBr pellet, cm⁻¹): 2923, 1606, 1546, 1377, 1335, 1244, 1185, 1109, 1035, 995, 893, 809, 775, 727, 654. UV-Vis. (CH₂Cl₂, λ_{max} nm; ε, M⁻¹cm⁻¹): 496 (39880), 332 (15655), 300 (33852).

2.1e [Cu(4-nimpdpm)(acac)] (2): It was prepared following the above procedure for **1** using 4-nimpdpm (0.288 g, 0.001 mol) and Cu(acac)₂ (0.288 g, 0.001 mol). Yield: 35% (0.172 g). *Anal.* Calc. for C₂₃H₁₉N₅O₄Cu: C, 56.04; H, 3.88; N, 14.21%. Found: C, 56.24; H, 4.00; N, 14.33%. ESI-MS (*m/z*) obs (calcd.): 492 [M]⁺ (492). IR (KBr pellet, cm⁻¹): 2906, 1582, 1550, 1406, 1392, 1378, 1336, 1244, 1206, 1178, 1118, 1080, 1028, 994, 892, 818, 770, 732, 654. UV-Vis. (CH₂Cl₂, λ_{max} nm; εM⁻¹cm⁻¹): 490 (39764), 320 (15770), 233 (21567).

2.1f [Cu(4-nimpdpm)(hfacac)] (3): It was synthesized adopting the above procedure for **1** using 4-nimpdpm and Cu(hfacac)₂·2H₂O. Yield: 28% (0.168 g). *Anal.* Calc. for: C, 46.00; H, 2.18; N, 11.65%. Found: C, 45.88; H, 2.32; N, 11.79%. ESI-MS (*m/z*) obs (calcd.): 600 [M]⁺, (600). IR (KBr pellet, cm⁻¹): 2923, 1648,

1552, 1456, 1408, 1378, 1340, 1302, 1248, 1212, 1146, 1114, 1064, 1034, 1000, 964, 890, 818, 778, 672. UV-Vis. (CH_2Cl_2 , λ_{max} nm; $\epsilon\text{M}^{-1}\text{cm}^{-1}$): 491 (32945), 318 (17354), 230 (22142).

2.1g $[\{\text{Cu}(4\text{-bimdpdm})(\text{acac})\}_n]$ (**4**): This compound was prepared following the above procedure for **1** using 4-bimdpdm and $\text{Cu}(\text{acac})_2$ in 1:1 molar ratio. Yield: 33% (0.232 g). *Anal.* Calc. for $\text{C}_{28}\text{H}_{25}\text{N}_5\text{O}_2\text{Cu}_2$: C, 56.94, H, 4.27; N, 11.86%. Found: C, 56.78; H, 4.23; N, 11.79%. ESI-MS (m/z) obs (calcd.): 498 $[\text{M}]^+$ (498). IR (KBr pellet, cm^{-1}): 2925, 1649, 1550, 1450, 1406, 1376, 1340, 1305, 1246, 1213, 1146, 1113, 1065, 1034, 1003, 965, 895, 816, 778, 675. UV-Vis. (CH_2Cl_2 , λ_{max} nm; $\epsilon\text{M}^{-1}\text{cm}^{-1}$): 496 (22 245), 298 (19180), 231 (18605).

2.1h $[\{\text{Cu}(4\text{-bimdpdm})(\text{hfacac})\}_n]$ (**5**): It was prepared following the above procedure for **1** using 4-bimdpdm and $\text{Cu}(\text{hfacac})_2 \cdot 2\text{H}_2\text{O}$ in 1:1 molar ratio. Yield: 28% (0.168 g). *Anal.* Calc. for $\text{C}_{28}\text{H}_{19}\text{Cu}_2\text{F}_6\text{N}_5\text{O}_2$: C, 48.14; H, 2.74; N, 10.03%. Found: C, 48.16; H, 2.72; N, 10.04%. ESI-MS (m/z) obs (calcd.): 606 $[\text{M}+\text{H}]^+$ (606). IR (KBr pellet, cm^{-1}): 2926, 1646, 1555, 1525, 1460, 1408, 1382, 1342, 1257, 1209, 1147, 1114, 1032, 1036, 1000, 799, 744, 672. UV-Vis. (CH_2Cl_2 , λ_{max} nm; $\epsilon\text{M}^{-1}\text{cm}^{-1}$): 502 (12592), 468 (25092), 340 (09536), 232 (17698).

2.2 X-ray crystallography

Preliminary data on the space group and unit cell dimensions as well as intensity data for **1** and **3** were collected on OXFORD DIFFRACTION X CALIBUR-S and for **4** on a Bruker APEX II with $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods and refined using SHELX-97.³⁵ Non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were geometrically fixed and refined using a riding model. Computer program PLATON was used for analysing the interaction and stacking distances.³⁶ CCDC-789391 (**1**), 789392 (**3**) and 832184 (**4**) contains supplementary crystallographic data for this paper. It can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from CCDC, 12 Union Road, Cambridge CB21EZ, UK; Fax: + 44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

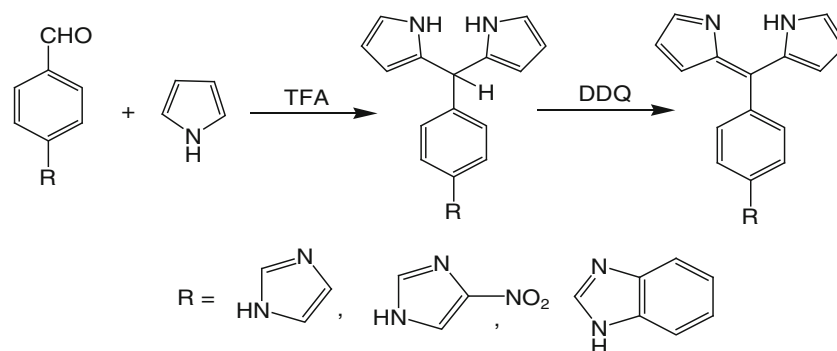
3.1 Synthesis

The aldehydes 4-imidazol-1-yl-benzaldehyde, 4-(4-nitro-imidazol-1-yl)-benzaldehyde, and 4-benzimidazol-1-yl-benzaldehyde were prepared by the reaction of 4-fluorobenzaldehyde with imidazole, 4-nitroimidazole and benzimidazole, respectively following literature procedure with slight modifications (see Supplementary Information).³³ Condensation of the respective aldehydes with pyrrole in the presence of catalytic amounts of TFA (0.1 mM) afforded 5-(4-imidazol-1-yl-phenyl)-dipyrromethane, 5-(4-nitro-imidazol-1-yl-phenyl)-dipyrromethane and 5-(4-benzimidazol-1-yl-phenyl)-dipyrromethane in reasonably good yields.²⁸ Although, the synthesis of 5-(4-imidazol-1-yl-phenyl)-dipyrromethane has already been reported²² we prepared this compound adopting a different method. The synthesis of dipyrrens were achieved by oxidation of respective dipyrromethanes using DDQ in a mixture of benzene and dichloromethane.^{28,37} A simple route for the synthesis of dipyrromethanes and corresponding dipyrrens is depicted in scheme 1. The dipyrrenato complexes **1–5** were obtained in good yield by *in situ* reaction of dipyrrens with metal precursors (scheme 2a, b).

The reaction of $\text{Cu}(\text{hfacac})_2 \cdot 2\text{H}_2\text{O}$ with 4-impdpdm (1:1 molar ratio) gave a trinuclear complex $[\text{Cu}_3(\text{hfacac})_4(4\text{-impdpdm})_2]$ **1**, while mononuclear complexes $[\text{Cu}(\text{acac})(4\text{-nimpdpdm})]$ **2**, and $[\text{Cu}(\text{hfacac})(4\text{-nimpdpdm})]$ **3** were obtained from the reactions of $\text{Cu}(\text{acac})_2/\text{Cu}(\text{hfacac})_2 \cdot 2\text{H}_2\text{O}$ with 4-nimpdpdm under analogous conditions. On the other hand, 4-bzimpdpdm reacted with $\text{Cu}(\text{acac})_2/\text{Cu}(\text{hfacac})_2$ to afford 1D polymers $[\{\text{Cu}(4\text{-bimdpdm})(\text{acac})\}_n]$ **4** and $[\{\text{Cu}(4\text{-bimdpdm})(\text{hfacac})\}_n]$ **5**. The complexes **1–5** are air-stable, crystalline solids, soluble in common organic solvents viz., dichloromethane, chloroform, acetone, acetonitrile, dimethylsulphoxide, dimethylformamide and insoluble in water, methanol, diethyl ether, petroleum ether, *n*-hexane, benzene and toluene. The characterization of dipyrromethanes and complexes **1–5** have been achieved by satisfactory elemental analyses, and spectral (IR, mass, electronic absorption and emission) studies.

3.2 Spectral studies

The infra red spectral data of **1–5** is summarized in experimental section alongwith other characterization data of the complexes. IR spectra of the complexes

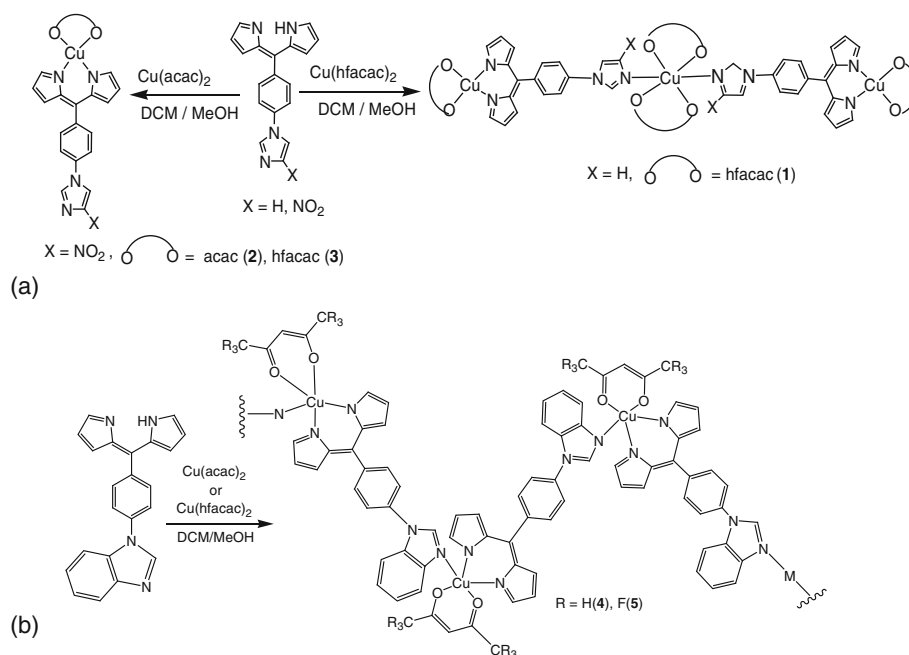


Scheme 1. Synthesis of dipyrins.

under study displayed bands at $\sim 1546\text{ cm}^{-1}$ assignable to $\nu_{\text{C}=\text{Npyr}}$. Alongwith $\nu_{\text{C}=\text{Npyr}}$ vibrations **1**, **3** and **5** exhibited bands due to $\nu_{\text{C}=\text{O}hfacac}$ at $\sim 1648\text{ cm}^{-1}$. Similarly, the complexes containing acac (**2** and **5**) displayed bands at $\sim 1588\text{ cm}^{-1}$ assignable to $\nu_{\text{C}=\text{O}acac}$.^{20–22,38} The IR spectral data supported formation of the respective complexes.

The electronic absorption and emission spectra of **1–5** were acquired in dichloromethane and resulting data is summarized in table 3. In its UV-vis. spectra, **1–4** displayed intense low energy transitions at $\sim 495, 492, 491$ and 496 nm alongwith high energy bands at $\sim 332, 300$ (**1**), $320, 233$ (**2**), $318, 230$ (**3**), $298, 230$ (**4**). Complex **5** displayed low energy bands at 502 and 468 nm , while high energy transitions appeared

at 340 and 233 nm . Intense low-energy transitions in the spectra of respective complexes have been assigned to charge-transfer processes associated with dipyrin ligands^{25–28} and bands in the region $\sim 230–340\text{ nm}$ have been assigned to the ligand centred intra-ligand transitions.^{39,40} The complexes **1–3** are non-fluorescent at room temperature, while **4–5** display weak fluorescence.⁴¹ The non fluorescent behaviour of **1–3** can be ascribed to the MLCT (metal to ligand charge transfer) transitions from paramagnetic Cu(II) core to π -chromophore of the respective ligands along with its intrinsic quenching nature.⁴² In contrast, weak fluorescence displayed by **4** (572 nm) and **5** (555 nm) may be attributed to the extended conjugation in 4-bimdpdm relative to 4-impdpdm, which dominates over MLCT



Scheme 2. Synthesis of complexes **1–5**.

transitions in copper (II) complexes. Stronger fluorescence of **5** in comparison to **4** may be related to the presence of electron withdrawing hfacac as a co-ligand instead of acac.

3.3 Magnetic measurements

The room temperature (28.2°C) magnetic moment (μ_{eff}) of the complexes were found to be 2.12 (**1**), 2.18 (**2**), 2.13 (**3**), 1.98 (**4**) and 1.95 B.M (**5**). These fall in the range for spin only value (1.70–2.20), suggesting that the metal centre in these complexes contains one unpaired electron and supported the formation of Cu(II) complexes.

3.4 Description of the crystal structures

Structures of **1**, **3** and **4** have been authenticated crystallographically. Details about the data collection and refinement are gathered in table 1. Selected geometrical parameters are summarized in table 2 and crystal structures depicted in figures 1, 2 and S6 (Supporting information figure S6). Heteroleptic trinuclear complex **1** contains three copper centres bonded to each

other through bridging dipyrin ligand. The immediate coordination geometry about Cu2 centre is octahedral and defined by four oxygen donors from two independent hfacac co-ligands and imidazolyl nitrogens from two different 4-impdpm ligands (figure 1). On the other hand, Cu1/ Cu1_1 centres displayed distorted square-planar geometry defined by two oxygen donors from hfacac, and the pyrrolyl nitrogens of the 4-impdpm. The Cu–N and Cu–O bond distances about the square planar Cu(II) centres are in the range of 1.912–1.923 Å and 1.955–1.956 Å, respectively. The N(O)–Cu–N(O) bond angles fall in the range of 90.12–93.24° (table 2).^{20–22,38} The angle (ω) between CuO₂ and CuN₂ planes has been found to be 25.14°, which clearly suggested distortion from regular square planar geometry. The Cu–N and Cu–O bond distances about the octahedral Cu2 are slightly longer in comparison to the square planar Cu(II) centres (table 2). The Cu–O (hfacac) bonds distances are not identical, it shows one short (Cu2-O3/Cu2-O3_3, 2.003 Å) and one long (Cu2-O4/Cu2-O4_4, 2.259 Å) bond. The observed elongation of the bond distances may be ascribed to the Jahn–Teller distortion.

Complex **3** crystallizes in monoclinic system with $P2_1/c$ space group. The immediate coordination geometry about Cu(II) in this complex is distorted square

Table 1. Crystal data and structure refinement parameters for **1**, **3** and **4**.

	1	3	4
Empirical formula	C ₅₆ H ₃₀ F ₂₄ N ₈ O ₈ Cu ₃	C ₂₃ H ₁₃ F ₆ N ₅ O ₄ Cu	C ₂₁ H ₁₇ Cu ₁ N ₃ O ₁
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	15.6718(10)	29.8569(6)	8.6919(13)
<i>b</i> (Å)	17.1682(13)	11.2531(3)	15.754(2)
<i>c</i> (Å)	18.6430(14)	6.6573(2)	16.664(3)
α (deg)	64.257(7)	90.00	90.00
β (deg)	73.389(6)	95.222(2)	90.00
γ (deg)	79.259(6)	90.00	90.00
<i>V</i> (Å ³), <i>Z</i>	4318.4(5), 2	2227.45(10), 4	2281.9(6), 5
λ (Å)	0.71073	0.71073	0.71073
Colour and habit	Orange, block	Red, thin-plate	Red, needle
<i>T</i> (K)	150(2)	150(2)	293(2)
Reflns collected	32866	10536	14949
Reflns/restraint/params	15170/0/1339	3907/0/352	5596/0/310
<i>D</i> _{calcd} (Mg m ⁻³)	1.834	1.792	1.450
μ (mm ⁻¹)	1.240	1.076	0.990
GOF on <i>F</i> ²	0.810	1.032	1.054
Final <i>R</i> indices <i>I</i> > 2 σ (<i>I</i>) ^a	R1 = 0.0426 wR2 = 0.0872	R1 = 0.0282 wR2 = 0.0774	R1 = 0.0516 wR2 = 0.1050
<i>R</i> indices (all data) ^a	R1 = 0.0922	R1 = 0.0351 wR2 = 0.0790	R1 = 0.0823 wR2 = 0.1297

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

Table 2. Selected bond lengths (Å) and angles (°) for **1**, **3** and **4**.

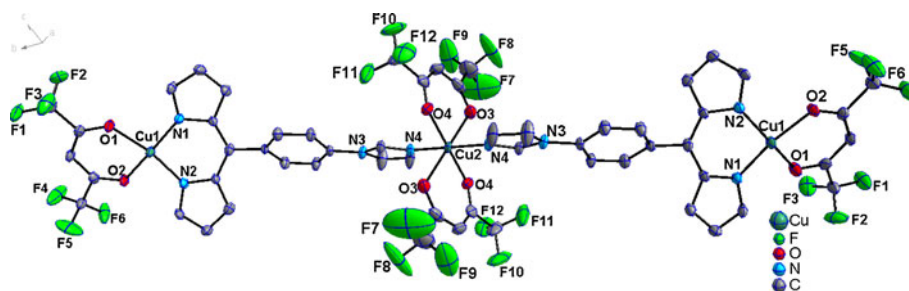
		Bond lengths		Bond angles	
Complex 1	Cu1–N1	1.912(3)	N2–Cu1–N1	93.24(13)	
	Cu1–N2	1.923(3)	O2–Cu1–O1	90.12(11)	
	Cu1–O1	1.956(3)	O1–Cu1–N1	91.36(12)	
	Cu1–O2	1.955(3)	O1–Cu1–N2	158.81(14)	
	Cu2–N4_4	1.982(3)	N4–Cu2–N4_4	180.000(1)	
	Cu2–N4_4	1.982(3)	O3–Cu2–N4	88.10(12)	
	Cu2–O3	2.003(3)	O3–Cu2–O4	87.89(12)	
	Cu2–O3_3	2.003(3)	O3–Cu2–O4_4	92.11(12)	
	Cu2–O4	2.259(3)	O3–Cu2–O3_3	180.00(15)	
	Cu2–O4_4	2.259(3)			
		ω 25.14			
Complex 3	Cu1–N1	1.935(17)	N2–Cu1–N1	92.95(7)	
	Cu1–N2	1.926(17)	O2–Cu1–O1	88.92(6)	
	Cu1–O1	1.954(14)	O1–Cu1–N1	89.78(7)	
	Cu1–O2	1.951(15)	O1–Cu1–N2	174.94(7)	
	N5–O3	1.235(2)			
	N5–O4	1.219(2)			
		ω 7.91			
Complex 4	Cu1–N1	1.994(3)	N2–Cu1–N1	90.53(13)	
	Cu1–N2	1.959(3)	O2–Cu1–O1	90.14(13)	
	Cu1–O1	1.974(3)	O1–Cu1–N1	154.97(13)	
	Cu1–O2	1.951(3)	O1–Cu1–N2	177.86(13)	
	Cu1–N4	2.349(3)	O2–Cu1–N4	92.27(12)	
			N2–Cu1–N4	89.60(13)	
			O1–Cu–N4	104.28(12)	
			N1–Cu1–N4	100.66(12)	
			ω 25.09		

ω = Angle between CuO2 and CuN2 planes

planer and completed by two oxygen (O1, O2) from the co-ligand hfacac and two nitrogen donors (N1, N2) from 4-nimdpdm in *bis*-chelating manner. The distortion from ideal square planar geometry has been estimated from interplanar angle (ω) between the planes containing N(1)-Cu(1)-O(2) and N(2)-Cu(1)-O(1) which falls to be 84.25°. The Cu–N bond distances are comparable to the Cu–N separations in other related systems.^{20–22,38} Further, the Cu–N distances are slightly smaller, while Cu–O_{hfacac} distances are slightly

longer in comparison to **1** having hfacac as an ancillary ligand. The bond angles N1–Cu–N2, O1–Cu–O2 are 92.95 and 88.92°, respectively. The angle between CuO₂ and CuN₂ (ω) planes is 7.91°, which further suggested distortion from square planar geometry.

The polymeric complex **4** crystallized in orthorhombic system with P_{212121} space group. Asymmetric unit contains two Cu(II), one 4-bzimdpdm ligand and one acac group. Two Cu(II) centres are separated by 4-bzimdpdm spacer with a Cu···Cu distance of 13.88 Å.

**Figure 1.** Crystal structure of **1** (hydrogen atoms omitted for clarity).

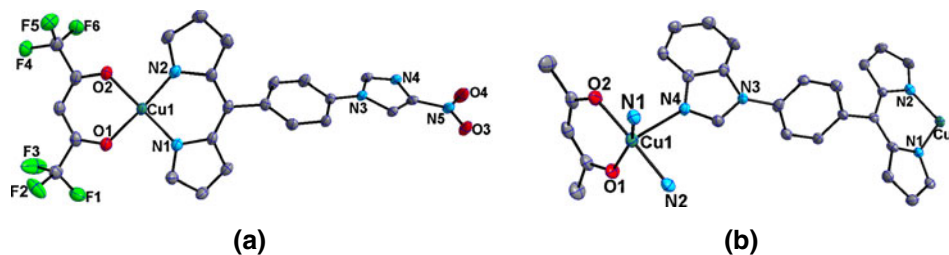


Figure 2. Crystal structure of **3** (a) and **4** (b) hydrogen atoms omitted for clarity.

A 1D linear polymeric chain is constructed upon extending the asymmetric unit. The copper (II) centres in the polymeric chain adopted distorted square pyramidal geometry defined by two oxygen donors from acac, two nitrogens from 4-bzimpdp and the *meso*-benzimidazolyl nitrogen. Three Cu(II) centres in 1D polymeric chain oriented in such a way that it generates isosceles triangle with side distances of $13.192 \times 13.192 \times 15.754 \text{ \AA}$. The interplanar angle (ω) between plane containing N(1)-Cu(1)-O(1) and N(2)-Cu(1)-O(2) is 89.05° , which is very close to the ideal angle of 90° . It strongly suggested that the donor sites [N(1), N(2), O(1) and O(2)] lie in the same plane. The Cu-N bond distances are comparable to the values reported in literature.^{20-22,38} The Cu-N (benzimidazolyl) bond distances are 2.349 \AA . The Cu-N and Cu-O bond distances are relatively longer than those in **1** and **2**. The bite angles N1-Cu-N2, O2-Cu-O1, O2-Cu-N4, N2-Cu-N4, O1-Cu-N1, and O1-Cu-N2 suggested slightly distorted square pyramidal geometry about the Cu(II) centre (table 2).

3.5 Supramolecular assemblies through weak interactions

The weak interaction studies revealed the presence of various types of weak interactions leading to interesting motifs. Complex **1** displayed C-H \cdots O (3.615 \AA) and C-H $\cdots\pi$ ($3.57\text{--}3.74 \text{ \AA}$) interactions leading to formation a bi-layer structural motif (figure S7). The outer layer of this motif consists of hfacac fragments, wherein molecules have anti-parallel arrangement. In complex **3**, C-F $\cdots\pi$ (3.14 \AA), C-H $\cdots\pi$ (3.61 \AA), $\pi\cdots\pi$ ($3.29\text{--}3.37 \text{ \AA}$) interactions lead to ladder like motif (figure S8), while C-H \cdots O (2.89 \AA), C-H \cdots N (3.10 \AA) and C-H $\cdots\pi$ (3.48 \AA) interactions in **4** are involved in the creation of π independent infinite 1D polymer (figure S9).

4. Conclusion

Through this contribution we have presented three novel *meso*-substituted dipyrinato ligands, and heteroleptic complexes $[\text{Cu}_3(4\text{-impdp})_2(\text{hfacac})_4]$, $[\text{Cu}(4\text{-nimpdp})(\text{acac})]$, $[\text{Cu}(4\text{-nimpdp})(\text{hfacac})]$, $[\{\text{Cu}(4\text{-bimpdp})(\text{acac})\}_n]$, and $[\{\text{Cu}(4\text{-bimpdp})(\text{hfacac})\}_n]$, based on it. The Cu(II) complexes impart acetylacetonato (acac) and hexafluoroacetylacetonato (hfacac) groups as ancillary ligands. It has been observed that proper functionalization of heteroditopic dipyrinates can lead to a variety of extended architectures upon interaction with $\text{Cu}(\text{acac})_2$ and $\text{Cu}(\text{hfacac})_2 \cdot \text{H}_2\text{O}$. Further, it has been demonstrated that the *meso*-substituent influences optical properties of the resulting complexes. This approach seems promising for the development of novel heteroleptic complexes.

Supplementary materials

X-ray crystallographic files in CIF format. Preparation of aldehydes, ESI-MS of **1-5** and some interesting motifs resulting from weak interactions in **1**, **3** and **4** are given as electronic supplementary information. Helical 1D chain structure of **4** (S6), UV-vis and fluorescence spectra of **1-5** (S10) and table for photophysical properties of **1-5** (table S1). For details, see www.ias.ac.in/chemsci website.

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