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Spacer length dependent architectural diversity in bis-dipyrrin copper(II) complexes

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A series of copper(II) complexes (1–9 and 3') derived from bis-dipyrrin ligands (L1–L9 and L3') with diverse spacer lengths $[-(CH_2)_n-]$ have been described. Structural diversity in these complexes have been explicitly established by spectral and structural studies on these and a closely related nickel(II) complex (3"). All the ligands and complexes have been thoroughly characterized by spectroscopic studies (ESI-MS, IR, ¹H, ¹³C NMR, UV/vis) and structures of 2, 3', 3", 6, 8 and 9 determined by X-ray single crystal analyses. It has been unambiguously established that ligands with $n \le 6$ gave heteroleptic binuclear (1–5), while those with $n \ge 7$ yielded homoleptic mononuclear (6–9) bis-dipyrrinato complexes. Spectral and structural studies revealed distorted square planer (1–5) and distorted tetrahedral geometry (6–9) about the copper(II) centre in these complexes which has further been evidenced by EPR and electrochemical studies. Structural differences based on odd and even number of methylene spacers in these complexes has been drawn on the basis of limiting spacer length.

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Introduction

Published on 24 March 2017. Downloaded by University of Newcastle on 25/03/2017 10:02:30.

Rational design and synthesis of supramolecular architectures with exciting properties via complexation employing appropriate combination of the metal ion and ligands has been a theme of enormous interest in contemporary chemical research.¹⁻³ Among various types of ligands being used for this purpose, dipyrrins also known as dipyrromethenes have proved to be indispensable.⁴⁻⁷ Substantial current interest has also arisen towards development of multinuclear metal complexes involving oligodipyrrins or the ligands having multiple dipyrrin units linked by a variety of spacers capable of forming well defined architectures upon coordination with the metal ions via self-assembly processes.⁸⁻¹⁶ Further, considering the importance of copper(II) complexes in magnetochemistry and materials science a variety of dipyrrin ligands and their copper(II) complexes including supramolecular systems have been developed and extensively studied.¹⁷⁻²³ In addition, polynuclear copper(II) complexes have attracted the attention of scientific community due to their usage in extending our knowledge on molecular features influencing the nature of exchange coupling between neighbouring metal centres via involvement of the bridging ligands, their efficacy towards DNA cleavage, and relevance in metalloproteins.²⁴ As well, bis-dipyrrin metal complexes with double helical/triangular structures and conformationally flexible linkers have also been explored.^{13,25–32}

A number of reports dealing with bis-dipyrrins along with their copper and zinc complexes bearing rigid and flexible spacers ranging from esters, amides, methylene, alkynyl, particularly at α/β position of the pyrrole are available in the literature.^{5,25–41} However, those involving rotatable *meso-* position as locus for the spacers with a well defined strategy for achieving bisdipyrrin based mono- and binuclear complexes by varying spacer lengths have not been reported. Moreover, porphyrins also considered as cyclic bis-dipyrromethenes are highly attractive and have been employed in the development of numerous supramolecular systems.⁴² It has been categorically shown that expansion or contraction of the porphyrin core leads to variation of the spin state of the metal centre.^{43–44} This observation and the proven flexibility of the methylene –(CH₂)_n– spacers have prompted us to explore this prospect in bis-dipyrrin based complexes. Apparently, nuclearity in these complexes can be controlled by varying the chain length between *meso-* substituted phenyl ring at *ortho* relative to *meta* or *para* position due to folding of the *ortho* substituted ligands under steric crowding. Further, spacer length dependent folding of the

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bis-dipyrrins may bring the coordinated metal centres at mutually interacting distance which, in turn, could facilitate exchange coupling between them.

Although, numerous dipyrrinato complexes have been synthesized and extensively studied, those based on dipyrrins imparting two chelating units separated by methylene spacers $(-(CH_2)_n-)$ have not been reported. With an intent to investigate the architectural and conformational limitations in spacer length directed fabrication of mono- and binuclear bisdipyrrin complexes some new dipyrromethanes (L1–L9, L3') with two N,N- donor bis-chelating units separated by *ortho* substituted $-(CH_2)_n-$ spacers have been synthesized. Effect of the *ortho* substitution has also been realized by synthesizing bis-dipyrrins with *para* substituted $-(CH_2)_n-$ spacers (L3'). Through this work, we describe synthesis and characterization of L1–L9, L3' having two *meso-*2/4-phenoxy substituted dipyrrin units linked by $-(CH_2)_n-$ spacers and their reactivity with Cu(acac)₂, Cu(OAc)₂ and Ni(dtc)₂ under varying conditions affording binuclear copper(II) (1–5, 3'), nickel(II) (3'') and mononuclear copper(II) complexes (6–9). Prominent role of the spacer length directed architectural distinction on photophysical and electrochemical behavior of the mono- and binuclear copper(II) complexes have also been evaluated by theoretical studies.

Experimental section

Reagents

All the synthetic manipulations have been performed in deaerated solvents under nitrogen atmosphere. Solvents were purified by standard literature procedures prior to their use.⁴⁵ 2-hydroxybenzaldehyde, 1,2-dibromo derivatives (1,2-dibromoethane/-propane/-butane/-pentane/-hexane-/-heptane/-octane/-nonane/-decane), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), pyrrole, tetrabutyl ammonium perchlorate [(*n*-Bu)₄N]ClO₄, Cu(acac)₂ and anhydrous Cu(OAc)₂ were procured from the Sigma Aldrich Chemical Co. Pvt. Ltd., India and used as received.

General methods

Infrared and electronic absorption spectra were acquired on a Varian 3300 FT-IR and Shimadzu UV-1601 spectrophotometers, respectively. ¹H (300/500 MHz) and ¹³C (75/125 MHz) NMR spectra at room temperature were obtained on a JEOL AL300/500 FT-NMR spectrometer using tetramethylsilane [Si(CH₃)₄] as an internal reference. X-band EPR spectra were acquired

on a JEOL JES FA200 spectrometer calibrated with diphenylpicrylhydrazyl (DPPH; g = 2.0037). Electrospray ionization mass spectral (ESI-MS) data was acquired on a Bruker Daltonics-Amazon SL ion trap mass spectrometer. Electrochemical measurements were made on a CHI-620c electrochemical analyzer. The measurements were performed in a one compartment cell equipped with glassy carbon working, platinum wire counter, and Ag/Ag⁺ reference electrode under nitrogen atmosphere using tetrabutylammonium perchlorate [(*n*-Bu)₄N]ClO₄ as a supporting electrolyte.

Synthesis of the aldehydes (A1-A9). In a typical reaction, a solution of salicylaldehyde (0.244 g, 2.0 mmol) was treated with respective dibromo derivatives (1.0 mmol) and K_2CO_3 (0.276 g, 2.0 mmol) in DMF (20 ml) and the resulting reaction mixture heated overnight under reflux at 100 °C. It was subsequently poured into 200 mL of water and the precipitate thus obtained was filtered, thoroughly washed with water and dried in air.⁴⁶

Synthesis of bis-dipyrromethanes (L1–L9 and L3'). Aldehyde (10.0 mmol) [A1 (2.70 g); A2 (2.84 g); A3 (2.98 g); A4 (3.12 g); A5 (3.26 g); A6 (3.40 g); A7 (3.54 g); A8 (3.68 g), A9 (3.82 g) and A3' (2.98 g), respectively] and catalytic amounts of trifluoroacetic acid (15.4 μ L, 0.20 mmol) was added to an excess of degassed pyrrole (13.8 mL, 200.0 mmol) and the reaction mixture stirred overnight under nitrogen atmosphere.⁴⁷ After completion of reaction the contents of the flask were concentrated under reduced pressure and the obtained crude product was subjected to column chromatography over silica gel (SiO₂; hexane:ethylacetate, 8:2) to afford corresponding dipyrromethanes as a white solid (characterization data given in the Supplementary information).[†]

Synthesis of complexes (1-9 and 3'). In a typical reaction, DDQ (0.227 g, 1 mmol) dissolved in benzene (30 ml) was added drop wise with stirring to an ice cold solution of respective dipyrromethanes (L1–L9 and L3') (0.50 mmol) in CH_2Cl_2 (50 mL) over 1 h. It was stirred for an additional 1 h and after completion of the reaction (monitored by TLC) solvent was removed under reduced pressure. Resulting residue was re-dissolved in $CH_2Cl_2/MeOH$ (70 mL; 1:1 v/v) and filtered. This filtrate was successively treated with triethylamine (1.0 mL) and solid $Cu(acac)_2$ (0.262 g, 1 mmol for L1–L5, L3' and 0.131 g, 0.5 mmol for L6–L9) and the reaction mixture further stirred for ~4 h at room temperature. Ensuing reaction mixture was concentrated under reduced pressure and the residue purified by column chromatography (SiO₂, Hexane:

 CH_2Cl_2 , 1:1) to afford the complexes **1-9** and **3'** as red solid. (Yield and characterization data for complexes have been given in the Supplementary information).[†]

Synthesis of complex 3" (Ni^{II} analogue of 3). It was prepared following the above procedure using Ni(dtc)₂ (0.364 g, 1 mmol) in place of Cu(acac)₂. Yield 42% (0.196 g). ESI-MS. (Calcd, found, *m/z*) 961.1483, 961.1282 [M + 2H + Na]⁺. ¹H NMR (CDCl₃, 300 MHz, δ ppm): 1.23 (s, 6H), 1.91 (s, 4H), 3. 75 (s, 4H), 5.49 (s, 4H), 6.14 (d, *J* = 2.7 Hz, 4H), 6.44 (d, *J* = 3.3 Hz, 4H), 6.92 (d, *J* = 8.4 Hz, 4H), 6.99 (d, *J* = 8.1 Hz, 4H), 7.16–7.38 (m, 14H). ¹³C NMR (CDCl₃, 75 MHz, δ ppm): 25.2, 25.4, 29.6, 68.0, 101.5, 112.7, 116.4, 119.4, 126.6, 129.7, 131.8, 134.9, 141.7, 147.4, 156.8, 186.8. IR (KBr pellets, cm⁻¹): 721, 988, 1030, 1506, 1530, 1586, 2854, 2923.

X-ray structure determinations

Crystals suitable for single crystal X-ray diffraction analyses were obtained by slow diffusion of hexane over dichloromethane (DCM) solution of the respective complexes. Single crystal X-ray diffraction data for 3' and 3" were collected on 'Bruker APEX-II CCD' and for 2, 6, 8 and 9 on OXFORD DIFFRACTION X CALIBUR-S. Structures were solved by direct methods (SHELXL-2014/7) and refined by full-matrix least square on F^2 (SHELXL-2014/7).⁴⁸ Crystal structure of 2, 6 and 9 was refined by using restraints. Owing to the prolate ellipsoid in crystal structure of 2, phenyl ring C atoms were refined without locating the H atoms on them. All non-H atoms were treated anisotropically. H-atoms attached to the carbon were included as fixed contribution and geometrically calculated and refined with the SHELX riding model. Computer program PLATON was used for analyzing the interaction and stacking distances.^{49–50} CCDC deposition Nos. 1536918, (2); 1505321, (3'); 1505322, (3''); 1505319, (6); 1505320, (7); 1505370, (9) contain supplementary crystallographic data for this paper.

Results and discussion

Dipyrromethanes employed in this study 1,2-bis(2-phenoxy)-ethane-bis-dipyrromethane (L1), 1,3-bis(2-phenoxy)-propane-bis-dipyrromethane (L2), 1,4-bis(2-phenoxy)-butane-bis-dipyrromethane (L3), 1,4-bis(4-phenoxy)-butane-bis-dipyrromethane (L3'), 1,5-bis(2-phenoxy)-pentane-bis-dipyrromethane (L4), 1,6-bis(2-phenoxy)-hexane-bis-dipyrromethane (L5), 1,7-bis-(2-phenoxy)-heptane-bis-dipyrromethane (L6), 1,8-bis(2-phenoxy)-octane-bis-dipyrromethane (L7), 1,9-bis(2-phenoxy)-nonane-bis-dipyrromethane (L8) and 1,10-bis(2-phenoxy)-decane-bis-

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dipyrromethane (L9) have been synthesized by treatment of the respective aldehydes (A1-A9 and A3') with an excess of pyrrole in presence of catalytic amounts of trifluoroacetic acid.⁴⁷ Simple synthetic strategy adopted for preparation of the dipyrromethanes L1–L9 is shown in Scheme 1a and L3' in Scheme 1b. These have further been oxidized to respective dipyrrins using an equimolar amount of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in benzene which *in-situ* reacted with appropriate metal precursors/salts to afford the complexes in reasonably good yields (Scheme 2).



Scheme 1. Showing synthesis of dipyrromethanes.



Scheme 2. Showing synthesis of the complexes 1–9 and 3".

A series of flexible bis-dipyrrin ligands which may acquire diverse conformations in presence of metal ions have been chosen for the present study. It is presumed that depending upon spacer length one may obtain complexes wherein two metal centres are held at mutually interacting distances. Notably, bis-dipyrrins containing up to six $-(CH_2)_n$ - spacers (n \leq 6) reacted with Cu(acac)₂ and afforded heteroleptic binuclear bis-dipyrrinato complexes (1-5). Conversely, those with relatively longer spacer (n > 7) afforded mononuclear complexes (6-9). It indicated that dipyrrins are somehow attuned with the spacer length *i.e.* with long spacers these underwent folding while shorter ones with considerable steric hindrance kept away from folding. This genre of spacer length dependent folding in bis-dipyrrinato complexes has been observed for the first time. On reaction with $Cu(acac)_2$ bis-dipyrrins based on L1–L5 and L3' gave heteroleptic binuclear complexes 1-5 and 3' however L6-L9, afforded mononuclear complexes (6-9) wherein both the binding units of bis-dipyrrin chelate coordinate with the same metal centre. On the other hand, binuclear heteroleptic structure for complexes with spacer lengths n < 6 has been authenticated by single crystal X-ray analysis of the complex 2; however crystals for 3, 4 and 5 could not be obtained. In this direction, a Ni^{II}-analogue of complex 3 (3") was synthesized by using Ni(dtc)₂ and authenticated its heteroleptic binuclear structure by single crystal X-ray analysis. Further, taking advantage of the analogous binding behavior of copper/nickel precursors with dipyrrins, binding modes in 1-5 has also been deduced using 3'' as a prototype.^{23,51–52}

The complexes under investigation are crystalline, non hygroscopic solids, stable at room temperature and soluble in common organic solvents such as chloroform, dichloromethane (DCM), acetonitrile (CH₃CN) and acetone (CH₃)₂CO. These have been thoroughly characterized by spectral (ESI-MS, IR, UV/vis, EPR), and electrochemical (CV) studies and structures of 2, 3', 3'', 6, 8 and 9 have been unequivocally determined by X-ray single crystal analyses.

IR spectra of the complexes displayed characteristic bands due to dipyrrin moiety at ~782, 937, 1020, 1275, 1355, 1415, 1531, 1552, 2923 cm⁻¹ and diagnostic $v_{C=0}$ vibrations of the coordinated acac [1577, 1; 1578, 2; 1578, 3; 1579, 4; 1580, 5 and 1578 cm⁻¹, Cu(acac)₂]. Oxidation of L1–L9 to the respective dipyrrins and subsequent coordination with the metal ions has further been supported by loss of the vibrations due to NH stretching in the IR spectra of

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1–9. Bands associated with both coordinated acac and dipyrrin moiety (**1–5**), and those only from dipyrrin (**6–9**) in the spectra of respective complexes strongly supported formation of the homo-/ heteroleptic dipyrrinato complexes.^{8–11,20–23}

Compounds L1–L9 (Fig. S1–S9[†]) and 1–9 (Fig. S10–S18[†]) have been characterized by ESImass spectral studies. ESI-mass spectra of 1–5 displayed peaks due to $[M + Na]^+$, besides these also displayed a regular increase of 14 in molecular ion peaks attributable to each –CH₂– unit which clearly suggested their respective formulations (Fig. S10–S14[†], Table 1). In a similar manner, **6–9** displayed molecular ion peaks due to $[M + H]^+$ along with an analogous increase in molecular ion peaks by 14 (–CH₂– units) (Fig. S15–S18[†]). The ESI-mass of model complexes **3'** and **3''** showed peaks due to $[M + H]^+$ and $[M + Na]^+$, respectively (Fig. S19–S20[†]).

Complex	Calcd./ Found	Molecular	Complex	Calcd./ Found	Molecular
		ion species			ion species
1	845.1281/845.1301	$[M + Na]^+$	6	630.2156/630.2048	$\left[M+H\right]^+$
2	859.1438/859.1412	$[M + Na]^+$	7	644.2213/644.2214	$\left[M+H\right]^+$
3	873.1594/873.1474	$\left[M + Na\right]^+$	8	658.2369/658.2349	$\left[M+H\right]^+$
4	763.1407/763.5030	$[M - acac]^+$	9	694.2345/694.2331	$[M + Na]^+$
5	901.1907/901.1893	$\left[M + Na\right]^+$	3'	873.1594/873.1443	$\left[M+H\right]^+$
			3″	961.1483/961.1282	$[M + Na]^+$

Table 1: Molecular ion peak for the complexes 1-9, 3' and 3".

To affirm the formula, purity and integrity of ligands and nickel(II) complex (**3**"), ¹H and ¹³C NMR spectra have been acquired in CDCl₃ at room temperature (Fig. S21–S29†). Notably, similar ¹H and ¹³C NMR spectral features are expected for L1–L9, therefore spectra of the representative compounds L3 and **3**" (Ni^{II} analogue of **3**) are described here (Fig. S30†). ¹H NMR spectra of L3 displayed signals due to aliphatic (δ 1.80 and 3.94 ppm), *meso* (δ 5.42 ppm), pyrrolic [δ 5.96, 6.14, 6.68 and 7.87 ppm (br, N<u>H</u>)] and aromatic protons (δ 6.82, 7.18 ppm). On the other hand, **3**" showed small downfield shift for the phenyl, pyrrolic and aliphatic protons with respect to L3 and loss of the *meso-* (–C<u>H</u>) and –N<u>H</u> protons. Aliphatic protons for **3**" exhibited an up-field shift relative to precursor complex Ni(dtc)₂. It clearly suggested oxidation

of L3 to respective dipyrrin and its subsequent complexation with the metal centre to afford 3". ¹H NMR spectra of L1–L9 displayed an analogous pattern where *meso* (–C<u>H</u> protons resonated at ~ δ 5.42 and –N<u>H</u> at ~ δ 7.91 ppm (br) indicating formation of the respective compounds. Associated aliphatic and aromatic protons resonated at their usual positions. Furthermore, ¹³C NMR spectra of ligands are consistent with the earlier reports and supported their formation with proposed formulations.^{37,47}

Electronic absorption spectroscopy

Electronic absorption spectra of L1-L9 and the complexes 1-9 have been acquired in CH₂Cl₂ (Fig. 1). Spectra for L1–L9 displayed weak bands due to π – π * transitions at ~275 nm (Fig. S31[†]). Complexes 1–9 too exhibited similar spectral features and displayed strong absorptions in the low energy region (493, 1; 492, 2; 492, 3; 491, 4; 493, 5; 468, 6; 469, 7; 468, 8 and 469 nm, 9) and two high energy bands (348, 298, 1; 349, 300, 2; 347, 299, 3; 348, 298, 4 and 349, 298 nm, 5; 365, 269, 6; 368, 271, 7; 365, 273, 8 and 364, 274 nm, 9). The low energy bands have been assigned to π - π * transitions associated with dipyrrin chromophores while high energy bands to ligand-centreed transitions (Fig. 1a).^{8-11,20-23} Further investigations indicated that $\pi - \pi^*$ transitions associated with the complexes 1-5 and 6-9, occurred at slightly different wavelengths (~492 and ~470 nm), as well, 6-9 showed a hump at ~502 nm. From the available data it may be concluded that in mononuclear complexes 6–9 the π - π * transitions due to dipyrrin moiety splitted into two and displayed a band in the low energy region ~470 nm and red shifted hump at ~502 nm. Most likely it occurred due to excitation coupling phenomenon known as "Davydov Splitting" (Fig. 1b).⁵³⁻⁵⁴ This type of splitting is usually observed in bis-dipyrrin tetrahedral complexes. Thus, significant differences in absorption profiles for 1-5 and 6-9 may be attributed to noticeable structural disparity. Further, Davydov Splitting in 6-9 clearly suggested tetrahedral geometry owing to formation of the mononuclear complexes. ^{8–11,20–23,53-54} Furthermore, dipyrrin units in the mononuclear complexes assume two different planes due to distorted tetrahedral structure whereas in binuclear complexes it adopted distorted square planer geometry having two units in the same plane which has further been supported by electrochemical studies (vide-infra).

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Fig. 1 UV/vis spectra of the complexes 1–5 (a) and 6–9 (b) in DCM (c, 10 μ M) at room temperature.

Crystal structures

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Diffraction quality crystals for 2, 6, 8, 9, 3' and 3" have been obtained by slow diffusion of hexane in dichloromethane solution of respective complexes (Fig. 2–3). Crystallographic refinement parameters and selected geometrical parameters are gathered in Tables 2–5. Complex 2 and 8 crystallize in monoclinic system with ' $P2_1/n$ ' and 'C1c1' space groups while 6 and 9 crystallize in orthorhombic system with 'Pbca' and 'P2_12_12_1' space groups, respectively.

The metal centre in complex **2** is found to be coordinated two nitrogen and oxygen atoms from dipyrrin and acetylacetonato moieties, respectively adopting a distorted square planar geometry with dihedral angles for the planes, N(1)–Cu(1)–N(2) and O(1)–Cu(1)–O(2) being 4.88°. The Cu–N and Cu–O bond lengths [Cu1–N1, 1.954; Cu1–N2, 1.955; Cu1–O1, 1.939; Cu1–O2, 1.938 Å] and angles N1–Cu1–N2 (91.40°), O1–Cu1–O2 (90.61°), N2–Cu1–O1 (89.34°) and N1–Cu1–O2 (88.79°) are comparable to other related systems.^{8–11,20–23}

On the other hand, complexes **6**, **8** and **9** adopt distorted tetrahedral geometry around the Cu^{II} -metal centre (Fig. 2) with all the four coordination sites occupied by pyrrolic nitrogens (N1, N2, N3 and N4) from the respective bis-dipyrrin ligands. Dihedral angles between the planes N(1)–Cu(1)–N(2) and N(3)–Cu(1)–N(4) are 51.13° (6), 47.04° (8) and 47.26° (9) indicating the ease of steric crowding in **6–9**. Cu^{II} complexes are known to favor square planar geometry but due to steric hindrance between the *ortho* substituted –(CH₂)_n– linker and dipyrrinato ligand distortion must have occurred and the complexes would not have favored planar structures but adopted a tetrahedral geometry. The Cu–N(dpm) bond distances in these complexes [Cu–N1,

1.938; Cu–N2, 1.969; Cu–N3, 1.939; and Cu–N4, 1.964 Å (**6**); Cu–N1, 1.954; Cu–N2, 1.943; Cu–N3, 1.957; Cu–N4, 1.955 Å (**8**); and Cu–N1, 1.954; Cu–N2, 1.945; Cu–N3, 1.931 and Cu–N4, 1.939 Å (**9**)] are comparable to those with other closely related systems.^{8–11,55–57} Similarly, bond angles around Cu^{II} [N1–Cu1–N2, 92.5; N1–Cu1–N4, 151.6; N2–Cu1–N3, 137.0 and N3–Cu1–N4, 92.6° (**6**); N1–Cu1–N2, 92.2; N1–Cu1–N4, 148.0; N2–Cu1–N3, 145.2 and N3–Cu1–N4, 91.8° (**8**); and N1–Cu1–N2, 91.4; N1–Cu1–N4, 144.1; N2–Cu1–N3, 149.0 and N3–Cu1–N4, 92.5° are comparable to those with other distorted tetrahedral complexes.^{8–11,55–57}



Fig. 2 Crystal structures of 2 (a) 6 (b), 8 (c) and 9 (d).

Further, it has been observed that with an increase in the chain length $-(CH_2)_n$ - between two dipyrrin units in the complexes **6**, **8** and **9**, dihedral angles for the planes N(1)–Cu(1)–N(2) and N(3)–Cu(1)–N(4) decreases due to expansion of the ring size causing lower steric repulsion and thereby degree of distortion is minimized.

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Model complex **3'** represents a simple binuclear complex crystallizes in monoclinic system with $'P2_1/n'$ space group. The metal centre in this complex is coordinated by two each of nitrogen and oxygen atoms from the dipyrrin unit and acetylacetonato moieties, respectively adopting a square planar geometry with dihedral angles for the planes, N(1)–Cu(1)–N(2) and O(1)–Cu(1)–O(2) being 2.67°. The Cu–N and Cu–O bond lengths [Cu1–N1, 1.965(3); Cu1–N2, 1.958(3); Cu1–O1, 1.935(3); Cu1–O2, 1.938(3) Å] and angles N1–Cu1–N2 (91.37°), O1– Cu1–O2 (90.81°), N2–Cu1–O1 (88.78°) and N1–Cu1–O2 (89.07°) are comparable to other related systems.^{8–11,20–23} The *meso*-phenyl substituent is twisted by an angle of 62° with respect to the dipyrrin moiety.



Fig. 3 Crystal structure of the model complexes 3' (a) and 3'' (b).

The Ni^{II} analogue of **3** *i.e.* model complex **3**" crystallizes in triclinic system with *P*–1 space group in which Ni^{II} adopts a distorted square planar geometry with two nitrogen from each dipyrrin and two sulphur atoms from the dithiocarbamate units with the dihedral angle of 3.80° between the N1–Ni1–N2 and S1–Ni1–S2 planes. Distortion from the square planar geometry around the Ni^{II}-centre may be attributed to small bite angles (N1–Ni–N2, 93.13 and S1–Ni–S2, 77.41°). The Ni–N bond distances [Ni1–N1, 1.903 (6); Ni1–N2, 1.882 (8) Å], Ni–S [Ni–S1, 2.208 (3); Ni1–S2, 2.182 (3) Å] and bond angles [N1–Ni1–N2 (93.13°), S1–Ni1–S2 (77.41°),

N1–Ni1–S1 (95.49°) and N2–Ni1–S2 (94.07°)] in the complex are comparable to the earlier reports.^{51–52} In this complex too, the *meso*-phenyl substituent is twisted by 65° from the dipyrrin core to greater extent relative to **3'** (vide-supra). It evidently proved that molecular folding are more pronounced in *ortho*-substituted dipyrrinato complexes than the *para*- ones; however, it becomes effective only if sufficient spacer length is involved in the complex *i.e.* from **6** (n=7).

Density functional theory calculations

To gain a deep insight into the spacer dependent architectural disparity in the complexes under investigation, DFT optimizations have been performed. Model structures for 1-5 and 7 have been designed by ChemBioDraw Ultra software and 3D views optimized by minimizing energy in MM2 mode of the same software. On the other hand, models for **6**, **8** and **9** have been directly taken from their single crystal X-ray data and subjected to optimization. Geometry optimization for the complexes under study has been carried out using GAUSSIAN 09 by B3LYP methods.⁵⁸



Fig. 4 DFT optimized structures of complex 4 (a) and complex 5 (b).

The metal centre Cu^{II} has been described by LANL2DZ basis set while non-metal atoms by 6-31G** and resulting coordinates optimized energetically.¹⁷ Calculated geometrical parameters such as bond lengths, bond angles and bond energies are consistent with the single crystal X-ray data (Table S1–S2†).

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Optimization on a series of model complexes for 1-9 clearly showed that homoleptic mononuclear complexes are quite achievable from n = 6 (complex 5) onwards. It affirmed that steric factors are not strong enough to resist folding/bending of the molecules to form homoleptic mononuclear complexes. Though, in line with other studies like UV/vis where complexes 1-5 and 6–9 exhibited different absorption profiles from one another, it can reasonably be stated that from complex 6 onwards (spacer length $n \ge 7$) homoleptic mononuclear complexes are created which is consistent with the experimental observations, too from single crystal X-ray data for $\mathbf{6}$, 8 and 9. So, it has to be assumed that spacer lengths n < 7 are not sufficient to withstand folded mononuclear homoleptic architectures. Herein, this factual assumption may be varified by DFT optimization studies to reveal the probable factor for this change in coordination modes on going from n = 6 to 7. It is an inherent tendency for 6 and 7 membered sp³-alkyl chains to acquire *anti*and syn configurations, respectively. The syn configuration (n = 7, complex 6) naturally tends to form homoleptic mononuclear while *anti*- (n = 6, complex 5) prefers to form heteroleptic binuclear complex due to their spatial orientations. However, it is logical only for the threshold value for 'n' (6-7) because the complexes with n < 6 and > 7 unequivocally attain heteroleptic and homoleptic coordination modes, respectively. It is supported by DFT optimization of complexes with n = 2 to 6 where all acquire only heteroleptic binuclear mode and confirmed by single crystal X-ray study for complex 2 which attains a heteroleptic binuclear structure irrespective of its syn configuration of alkyl chain (n = 3) (Fig. 4 and S32–S33⁺).

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The *syn* configuration thus supports the folding of the molecule to form mononuclear complex and apparently navigates the central metal to coordinate with both terminal dipyrrin cores simultaneously, to attain the mononuclearity. Similarly, for complexes with $n \ge 7$ *syn-anti* configuration factor also become meaningless most probably due to adequate flexibility in the molecule to acquire folded mononuclear architecture. Moreover, it is observed that after a certain specific chain length mononuclear homoleptic structure (**6-9**) are more stable relative to heteroleptic binulear complexes (**1-5**) which may be due to chelate effect of the ligand. After a certain chain length (n > 6), chelate effect predominate over steric hindrance which favors formation of mononuclear metallamacrocyclic structures. Therefore, one can have a clear-cut idea about the formation of complex depending on spacer length that mononuclear homoleptic complex begins to form with large spacer groups ($n \ge 7$) and the most probable factors responsible for transition from bi- to mononuclear complex formation are steric and *syn*-

conformation effects. The crystal structures of **8** and **9** with spacer lengths n = 9 and 10 respectively, also confirmed that these are engendered by reduced steric crowding in the systems relative to the dipyrrin complexes with $n \le 6$.

EPR spectral studies

EPR spectrum of the copper complexes in solution the provides useful information about environment around the metal centre. Data for complexes under investigation are presented in Table (S3[†]) and resulting spectra depicted in Fig. 5 and S34–35.[†] The X-Band EPR spectra of copper(II) complexes 1-9 were recorded in r.t CH₂Cl₂ solvent as well as in frozen solution at liquid nitrogen temperature (Fig. 2 and Table 1). The $g_{\parallel} > g_{\perp} > 2.003$ observed for the complexes are typical for d⁹ copper(II) and a ground state doublet indicating presence of the unpaired electron in a d_{x-y}^{2} orbitals.^{17,23–24} Room temperature X-band EPR for 1–5 displayed three line axial spectra due to merger of the third and fourth band. Solution state spectra in the complexes **6–9** show only one signal without any hyperfine splitting and a broadening of g_{\perp} , thus indicating severely distorted tetrahedral geometry, comparable to other related systems.^{17,23–24} On the other hand, spectra for 1–9 in frozen solution at liquid nitrogen temperature showed typical four line pattern expected from Cu(II) complexes. From the Fig. 5 and S34 we can see that the shape and the parameters of the EPR spectra of 1-5 and 6-9 are very similar, which indicate their similar coordination environments. The values of hyperfine coupling constant A_{ll} for 6–9 are quite low in comparison to the complexes 1–5. The factor $g_{\parallel}/A_{\parallel}$ offers a convenient empirical index for tetrahedral distortion in Cu(II) complexes, higher value of this factor for complexes 6-9 relative to 1-5 indicated greater distortion of the tetragonal site which has also been confirmed by the single crystal XRD study.



Fig. 5 EPR spectra of Complex 5 (a) and 6 (b) in CH₂Cl₂ solvent at liquid nitrogen temperature.

Electrochemical studies

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Electrochemical behavior of **1–9** have been investigated by cyclic voltammetry (CV) in CH₃CN (*c*, 100 μ M) using 0.1 M tetrabutylammonium perchlorate [(*n*-Bu)₄N]ClO₄ as a supporting electrolyte. Measurements have been made in the range of +1.5 to -2.0 V at a scan rate of 100 mVs⁻¹, and redox potentials referenced to Fc/Fc⁺ couple (0.1 V). Cyclic voltammograms of **1–5** exhibited one quasi-reversible oxidation wave (E_{pa} 0.680, **1**; 0.640, **2**; 0.630, **3**; 0.630, **4**; 0.620 V, **5**) assignable to oxidation of the dipyrrin moiety alongwith one irreversible (E_{pc1} -0.55, **1**; -0.53, **2**; -0.50, **3**; -0.51, **4**; -0.51 V, **5**) and one reversible reduction wave (E_{pc1} -1.26, **1**; -1.24, **2**; -1.23, **3**; -1.20, **4**; -1.18 V, **5**). On the other hand, **6–9** displayed two electron oxidation wave (E_{pa} 0.63, 0.77, **6**; 0.61, 0.75, **7**; 0.640, 0.818, **8**; 0.640, 0.818 V, **9**) assignable to oxidation of the dipyrrin moieties as well as one each of irreversible (E_{pc1} -0.48, **8**; -0.48 V, **9**) and reversible reduction wave (E_{pc1} -1.22, **6**; -1.20, **7**; -1.21, **8**; -1.20, V **9**).^{17,22,55-56,59} Weak irreversible reduction wave arises due to reduction of the dipyrrin moiety (Fig. 6 and S35–36, †).



Fig. 6 Cyclic voltammogram of 5 (a) and 6 (b) in CH₃CN (c, 100 μ M) at room temperature.

To affirm number of electrons involved in the redox process, chronocoulometric experiments have been performed on **5** and **6** as a representative of bi- and mononuclear complexes by determining their oxidation and reduction wave potentials (Fig. $S37-38^{+}$). It gave 1:1 ratio for

the number of electrons involved in oxidation and reduction processes. Therefore, it is concluded that oxidation and reduction of **5** and **6** is a two-electron process. The same conclusion could be drawn for other binuclear (1-4) and mononuclear copper complexes (7-9) as the shape of the voltammograms are similar in nature. In general, structural variations associated with a redox reaction induces a change in the redox potential. In square planer complexes 1-5, presence of two dipyrrin moieties in the same plane resulted coalescence of the first and second oxidation wave. On the other hand, as discussed earlier mononuclear complexes 6-9 adopted enforced tetrahedral coordination geometry and two dipyrrin moieties assume different planes, hence two distinct oxidation waves due to dipyrrin moieties. The above results corroborated well with the findings from single crystal X-ray diffraction analyses. This architectural dissimilarity further attested different spectral patterns in 1-5 as compared to 6-9.

Above studies clearly supported the formation of binuclear and mononuclear complexes in presence of ligands having identical dipyrrin terminals with variable number (n) of adjoining spacer units (-CH₂-). It has been demonstrated that complex 1-5 attain a binuclear heteroleptic architecture pertaining to the steric effects due to small chain lengths where 'n' varies from 2 from 6. Conversely, from complex **6** with n = 7, long chain spacers bring enough flexibility in the complexes so that steric effects become ineffective leading to formation of folded mononuclear homoleptic architecture. The folding at n = 7 has also been facilitated by the *syn* conformation of the complex which is attainable only with odd number of spacers as confirmed by DFT studies as well. The formation of bi-/mononuclear complexes with given number of spacers has further been supported by electrochemical and EPR studies. Thus, it may be concluded that such dipyrrin complexes may attain stable mononuclear architecture only if sufficient spacer chain lengths are provided.

Conclusion

In summary, through this work homo-/heteroleptic bis-dipyrrinato copper complexes have been synthesized by varying alkyl spacer length and their structural, optical, and electrochemical properties examined by various techniques. It has been noted that number of $-(CH_2)_n$ units in alkyl spacer directly influences the geometry and construct of resulting complexes. From single crystal X-ray and DFT studies it has been categorically shown that dipyrrins with spacer length n \leq 6 created a binuclear heteroleptic complex while those with n \geq 7 gave mononuclear homoleptic complexes. DFT studies additionally revealed that odd number of $-(CH_2)_n$ - units stabilizes *syn* conformation while even stabilizes *anti* conformation of the bis-dipyrrin complexes. The present work clearly demonstrated that position and length of the spacers between two dipyrrin units strongly influence the coordination behavior and supramolecular assembly of the dipyrrinato complexes. These observations can be further escalated in controlled designing of the supramolecular assemblies based on dipyrrin complexes.

Acknowledgements

Authors gratefully acknowledge financial support from the Department of Science and Technology (DST), New Delhi, India for providing financial assistance through the Scheme [SR/S1/IC-25/2011] and also to CSIR, New Delhi, India for the award of a senior Research Fellowship to RPP (No. 09/013(0514)/2013-EMR-I). We are also thankful to the Head, Departments of Chemistry, Institute of Science, Banaras Hindu University, Varanasi (U.P.) India, for extending laboratory facilities.

Supporting Information

¹H, ¹³C NMR, ESI-MS, and Tables are provided. CCDC No. 1536918, (**2**); 1505319, **6**; 1505320, **8**; 1505321, (**3'**); 1505322, (**3''**); 1505370, (**9**); contains the crystallographic data for this paper. It can be had free of charge *via* https://summary.ccdc.cam.ac. uk/structure-summary-form (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.; Fax: +44–1223–336033; Email: <u>deposit@ccdc.cam.ac.uk</u>).

9 2 6 8 Empirical formula $C_{43}H_{40}N_4Cu_2O_6$ $C_{37}H_{34}CuN_4O_2$ C39H38CuN4O2 $C_{40}H_{40}CuN_4O_2$ Crystal system monoclinic orthorhombic monoclinic orthorhombic 'P 2₁/n' C1c1 $P2_{1}2_{1}2_{1}$ Pbca Space group a (Å) 14.1141(3) 14.9525 (3) 25.9984(2) 8.9995(2) b (Å) 16.4924(3) 15.1818(3) 9.3703(2) 14.841(3) c (Å) 17.4915(3) 27.7558(5) 28.3965(8) 26.069(5)90.00 90.00 90.00 90.00 α (deg) 105.34(3) β (deg) 105.647(2)90.00 90.00 90.00 90.00 90.00 90.00 γ (deg) $V(Å^3), Z$ 3920.70(13), 4 6300.7(2), 27 6671.2(4), 8 3481.9(2), 4 λ (Å) 1.54184 0.71073 0.71073 0.71073 Color and habit Red, needle Green, block Green, block Green, block T (K) 293(2) 293(2) 293(2) 293(2) 26373 reflns collected 25906 55068 5658 7543/11/430 5539/9/397 5865/0/415 5658/5/401 refins/restraint/ params 1.416 1.329 1.311 1.283 D_{calcd} (g cm⁻³) $\mu \,({\rm mm}^{-1})$ 1.770 0.733 0.695 0.667 GOF on F^2 1.083 1.030 1.039 1.072 final *R* indices $I > 2\sigma(I)$ R1 = 0.1023R1 = 0.0544R1 = 0.0628R1 = 0.1298wR2 = 0.3137wR2 = 0.1378wR2 = 0.1247wR2 = 0.1460R indices (all data) R1 = 0.1312R1 = 0.0741R1 = 0.1219R1 = 0.3477wR2 = 0.3495wR2 = 0.1524wR2 = 0.1611wR2 = 0.1987

Table 2: Crystal data and structure refinement parameters for 2, 6, 8 and 9.

	3'	3″
Empirical formula	$C_{44}H_{42}Cu_2N_4O_6$	$C_{44}H_{48}N_6Ni_2O_2S_4\\$
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	P -1
<i>a</i> (Å)	7.2758(2)	9.531(5)
<i>b</i> (Å)	14.6438(6)	16.488(9)
<i>c</i> (Å)	18.4718(8)	16.546(9)
a (deg)	90.00	61.42(2)
β (deg)	91.52(3)	88.05(2)
$\gamma(\text{deg})$	90.00	79.41 (2)
$V(\text{\AA}^3), Z$	1967.4(2), 4	2240.0(2), 2
λ (Å)	0.71073	0.71073
Color and habit	Red, needle	Red, needle
<i>T</i> (K)	273(2)	301(2)
reflns collected	25113	4036
refins/restraint/	6593/0/ 264	6680/0/212
params		
$D_{\text{calcd}} (\text{g cm}^{-3})$	1.435	1.391
$\mu (\text{mm}^{-1})$	1.135	1.070
GOF on F^2	0.981	1.024
final <i>R</i> indices $I > 2\sigma(I)$	R1 = 0.0631	R1 = 0.0619
	wR2 = 0.1494	wR2 = 0.1189
<i>R</i> indices (all data)	R1 = 0.1732	R1 = 0.1436
	wR2 = 0.2148	wR2 = 0.1493

 Table 3: Crystal data and structure refinement parameters for 3' and 3".

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Bond length (Å)	2	Bond	6	8	9	
		length (Å)				
Cu–N1	1.954	Cu–N1	1.938	1.954	1.954	
Cu–N2	1.955	Cu–N2	1.969	1.943	1.945	
Cu–O1	1.939	Cu–N3	1.939	1.957	1.931	
Cu–O2	1.938	Cu–N4	1.964	1.955	1.939	
Bond Angle (°)			6	8	9	
N1–Cu1–N2	91.40°	N1-Cu1-N2	92.5	92.2	91.4	
O1–Cu1–O2	90.61	N1–Cu1–N4	151.6	98.1	97.3	
N2-Cu1-O1	89.34	N2-Cu1-N3	137.0	96.6	97.5	
N1-Cu1-O2	88.79	N3-Cu1-N4	92.6	91.8	92.5	

 Table 4: Selected bond lengths (Å) and angles (°) for 6, 8 and 9.

Table 5: Selected bond lengths (Å) and angles (°) for 3' and 3''.

Bond length (Å)	3'	Bond length (Å)	3″
Cu–N1	1.965	Ni–N1	1.903
Cu–N2	1.958	Ni–N2	1.882
Cu1–O1	1.935	Ni1–S1	2.208
Cu1–O2	1.938	Ni1–S2	2.182
Bond Angle (°)	3'	Bond Angle (°)	3″
N1–Cu1–N2	91.37	N1-Ni1-N2	93.13
O1–Cu1–O2	90.81	S1-Ni1-S2	77.41
N2-Cu1-O1	88.78	N1-Ni1-S1	95.49
N1–Cu1–O2	89.07	N2–Ni–S2	94.07

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Spacer length dependent architectural diversity in bis-dipyrrin copper(II) complexes

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Copper(II) complexes (1–9 and 3') derived from *bis*-dipyrrin ligands (L1–L9 and L3') with diverse spacer lengths $[-(CH_2)_n-]$ have been described. It has been noted that number of $-(CH_2)_n-$ units in alkyl spacer directly influence the geometry and construct of resulting complexes. Dipyrrins with spacer length $n \le 6$ created a binuclear heteroleptic complex while those with $n \ge 7$ gave mononuclear homoleptic complexes. A line between *syn-* and *anti-* conformation of the complexes has been drawn and based on it a limiting spacer length ($n \ge 7$) set for achieving mononuclear dipyrrin complexes.

Interoleptic Binuclear (1–5)