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# Regioselective Mannich bases of pyrrole-2-carbaldehyde and binuclear copper(II) complexes of bis(iminopyrrolyl) ligand containing the piperazine ring

Rajnish Kumar, Tapas Paul, Oishi Jana, Ganesan Mani *

*Department of Chemistry, Indian Institute of Technology-Kharagpur, Kharagpur, West Bengal 721 302, India*

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## ABSTRACT

Iminopyrrolyl ligands have attracted an attention in the field of coordination chemistry. As every iminopyrrolyl ligand contains at least one acidic pyrrole NH group, it often forms an anionic five-membered chelate ring with a metal. Unlike the familiar pincer framework ligand systems, iminopyrrolyl coordination chemistry is in a developing stage. Hence, we set the synthesis of bis(iminopyrrole) framework ligand containing the piperazine ring as a spacer unit between two mono(iminopyrrolyl) moieties. The Mannich reaction of pyrrole-2-carbaldehyde with piperazine and formaldehyde afforded two new dialdehydes: *N*,*N*′-bis(5-formylpyrrol-1-ylmethyl)piperazine **1** and *N*,*N*′-bis(5-formylpyrrol-2-ylmethyl)piperazine, **2**, which are regioselective products formed in good yields. The pyrrole N aminomethylated dialdehyde **1** was isolated in the absence of an added acid. Conversely, the pyrrole α-C aminomethylated dialdehyde compound **2** was obtained in the presence of a mineral acid. They have different spectroscopic and physical properties. Even they offered different Schiff bases under the same reaction conditions. The Schiff base condensation reaction of **2** with 2,6-diisopropylanilline in the presence of $HNO_3$ gave the expected [1+2] Schiff base in 53% yield after column separation. Conversely, the other dialdehyde **1** yielded the piperazinylmethyl C–N bonds hydrolyzed known 2-iminopyrrole compound. Further, the treatment of the structurally characterized [1+2] bis(iminopyrrolyl) ligand with copper(II) carboxylates $[Cu(OOCR)_2(H_2O)]$ (R = H, Me and Ph) gave three different binuclear five-coordinate copper(II) complexes. Their structures were determined by single crystal X-ray diffraction studies. Interestingly, the piperazine ring nitrogens are not coordinated, rather involved in intramolecular hydrogen bonding interactions with the coordinated solvent molecules at the copper atom.

## 1. Introduction

The mono(iminopyrrolyl) and bis(iminopyrrolyl) ligand systems possess an attractive coordination motif with metals, which drives their metal complexes synthesis [1]. Iminopyrrolyl ligands are conveniently synthesized by condensation reactions of the corresponding pyrrole aldehyde with a variety of primary amines, which have led to a variety of iminopyrrolyl ligands having varying steric and electronic properties [2]. In addition, ligands containing two iminopyrrole moieties linked through some aromatic or aliphatic spacer unit have also been developed [3]. Iminopyrrolyl metal complexes have been used as catalysts for ethylene polymerization [4] and the ring opening polymerization of ε-caprolactone [5] reactions. Similarly, a large progress has been made on the analogous bis(imino)dipyrromethanes and their coordination chemistry [6]. In addition, one of the noticeable features of metal complexes containing pyrrole based ligands is the binding mode of the pyrrolidine ring; it coordinates primarily in two modes: $\kappa^1$N (terminal) and $\eta^5/\kappa^1$N (bridging), which facilitate multinuclear complex formation [7].

Gmeiner and co-workers have reported the regioselective formylation of the piperazinylmethyl substituted pyrrole [8]. Keypour et al. have reported several Schiff bases containing the piperazine ring and studied their coordination chemistry [9]. In addition, Lee, Huang and co-workers have recently reported the mono- and dipiperazinylmethyl substituted pyrrole by the Mannich reactions of pyrrole [10]. We are interested in developing metal complexes of pyrrole-based ligand systems and their catalytic applications. Recently, we reported a few palladium complexes containing bis(iminopyrrolylmethyl)amine ligand, which shows an interesting amine–azafulvene tautomeric structure upon

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* Corresponding author. Fax: +91 3222 282252.
*E-mail address:* gmani@chem.iitkgp.ernet.in (G. Mani).

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complex formation, and their Suzuki cross coupling reactions [11]. These interesting properties of iminopyrrolyl ligands have made us to become interested in designing different iminopyrrolyl ligands for metal complexes study. Herein, we report two new regioselectively formed dialdehydes containing the piperazine ring as a spacer unit via the Mannich reaction of pyrrole-2-carbaldehyde. In addition, we also report synthesis and structural characterization of binuclear copper(II) complexes containing a new bis(iminopyrrolyl) ligand derived from the dialdehyde molecule.

## 2. Results and discussion

### 2.1. Synthesis and characterization of dialdehydes

Pyrrole-2-carbaldehyde reacts with a mixture of piperazine and formaldehyde in 2:1:2 molar ratios, respectively, to give the pyrrole N aminomethylated dialdehyde compound **1**, which was isolated as a colorless solid from the reaction mixture without further purification in 71% yield. Interestingly, when the same reaction was carried out in the presence of an acid, the pyrrole α-C aminomethylated dialdehyde compound **2** was obtained in almost the same yield as **1** (Scheme 1). Although the HRMS spectra of **1** and **2** showed the same molecular ion peak at *m*/*z* 301.1626 (calc. mass 301.1665) corresponding to their $[M+H^+]$ ions, these regioselectively formed products could be differentiated by NMR and IR methods. In the $^1H$ NMR spectrum of **1** in $CDCl_3$, the pyrrole ring CH resonances appeared as two multiplets at $\delta = 6.95$ and 6.23 ppm with their integrated intensity ratio of 2:1. In contrast, compound **2** showed the 1:1 integrated intensity ratio for the pyrrole ring CH protons which appeared as multiplets at $\delta = 6.89$ and 6.16 ppm; its pyrrolic NH resonance appeared as broad singlet at $\delta = 9.61$ ppm. Further, the N-bound methylene groups in **1** resonates as a sharp singlet at $\delta = 5.15$ ppm, which is shifted downfield by 1.59 ppm as compared to the resonance of the same group in **2** appearing at $\delta = 3.56$ ppm. Furthermore, this regioselectivity is supported by DEPT-135 spectra, which showed three signals for **1** and two signals for **2** for their pyrrole ring carbon atoms. Furthermore, the FT-IR spectrum of **2** displays the *ν*(NH) stretching frequency at 3239 $cm^{-1}$ appearing as a strong band, which is absent in the IR spectrum of **1**. These two compounds exhibit different physical properties; compound **1** is highly soluble in common organic solvents such as MeOH, $CHCl_3$, DCM, etc., whereas compound **2** is poorly soluble in these solvents. The pyrrolic N versus α-C regioselectivity could be explained in terms of acidity of the pyrrole-2-carbaldehyde NH group. In the absence of an added acid, the base-catalyzed Mannich reaction mechanism operates [12]. Thus, the piperazine probably abstracts the pyrrolic NH proton and resulting pyrrolidine anion attacks the in situ generated iminium ions present in the mixture to give the N-aminomethylated product. Conversely, in the case of acidic medium, the pyrrolic α-C is active and attacks the iminium ion to give the expected α-C aminomethylated product.

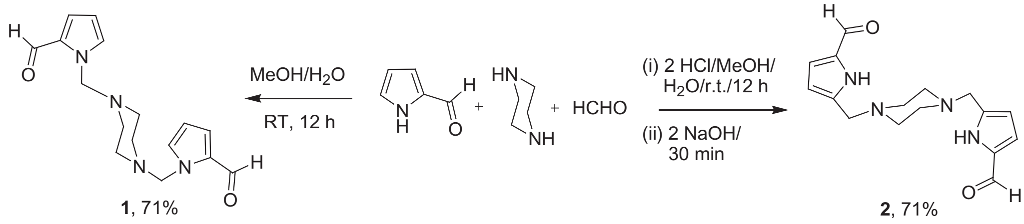
While our attempts to get suitable single crystals of compound **1** have failed, the structure of **2** was confirmed by single crystal X-ray diffraction analysis. The X-ray structure of **2** and the selected bond lengths and angles are given in Fig. 1 and Table 1, respectively. The two pyrrolyl moieties are bound in the equatorial positions of the chair conformation of the piperazine ring. While one of the pyrrolealdehyde moieties with its carbonyl O and the pyrrolic NH groups is oriented in one direction, the same groups in the other side of the molecule are oriented in an opposite direction. This results in four intermolecular hydrogen bonds between these groups for every molecule and formation of the 1D supramolecular chain structure in the crystal lattice (Fig. 1c). This is similar to the hydrogen bonding observed in the structure of *N*,*N*-di(α-formylpyrrolyl-α-methyl)-*N*-methylamine reported by us [13].

### 2.2. Synthesis and characterization of bis(iminopyrrolyl) ligand

Having synthesized the dialdehyde compounds containing the piperazine ring, we then set the synthesis of their open chain Schiff bases because such bases would provide two sets of donor atoms to a metal atom and give bimetallic complexes. The Schiff base condensation reaction of **2** with two equiv of 2,6-diisopropylaniline in the presence of two equiv of $HNO_3$ gave the [1+2] condensation product **3** and the partially hydrolyzed [1+1] product **4** in 53% and 20% yields, respectively, after column chromatographic separation (Scheme 2). Conversely, the analogous reaction using **1** resulted in the formation of the monoiminopyrrole compound **5** owing to the hydrolysis of the pyrrolic N–C bond on either side of molecule by nitric acid. While the compound **5** is a known compound [2b], compounds **3** and **4** are new compounds and characterized by spectroscopic methods.

The $^1H$ NMR spectrum of **3** features a sharp singlet at $\delta = 7.85$ ppm for the azomethine protons and at $\delta = 3.65$ ppm for the methylene protons. The pyrrolic NH resonance was not observed owing to an amine-azafulvene tautomeric structure, which forms upon transfer of the pyrrolic NH proton to the basic imine nitrogen atom. Analogous behavior has been reported for the other iminopyrrole molecules reported by us [11]. The FT-IR spectrum shows the *ν*(CH=N) stretching frequency at 1627 $cm^{-1}$. In addition, the molecular ion peak $[M+H^+]$ at *m*/*z* 619.4512 (calc. mass 619.4488) is observed in the HRMS spectrum. Conversely, the $^1H$ NMR spectrum of **4** features a broad resonance at $\delta = 9.82$ ppm which is assigned to the pyrrolic NH group located adjacent to the aldehyde group, while the other NH resonance does not appear owing to the amine–azafulvene tautomerism. The other resonances and their integrated intensity ratios are in accord with the structure of **4**. Besides, compound **4** shows the molecular ion peak at *m*/*z* 460.3111 (calc. mass 460.3076) corresponding to the mass of its $[M+H^+]$ ion in the HRMS spectrum.

The structure of the [1+2] Schiff base **3** was confirmed by the single crystal X-ray diffraction method (Fig. 2). The X-ray structure revealed the typical iminopyrrole form rather than the amine–azafulvene tautomeric structure, as shown by the N1–C13 (1.274(3) Å) and C13–C14 (1.432(4) Å) distances, corresponding to the double and single bonds, respectively. The molecule possesses two binding cavities for metal atoms. There is no bound water in



**Scheme 1.** Synthesis of the regioselective dialdehydes **1** and **2** containing the piperazine ring.

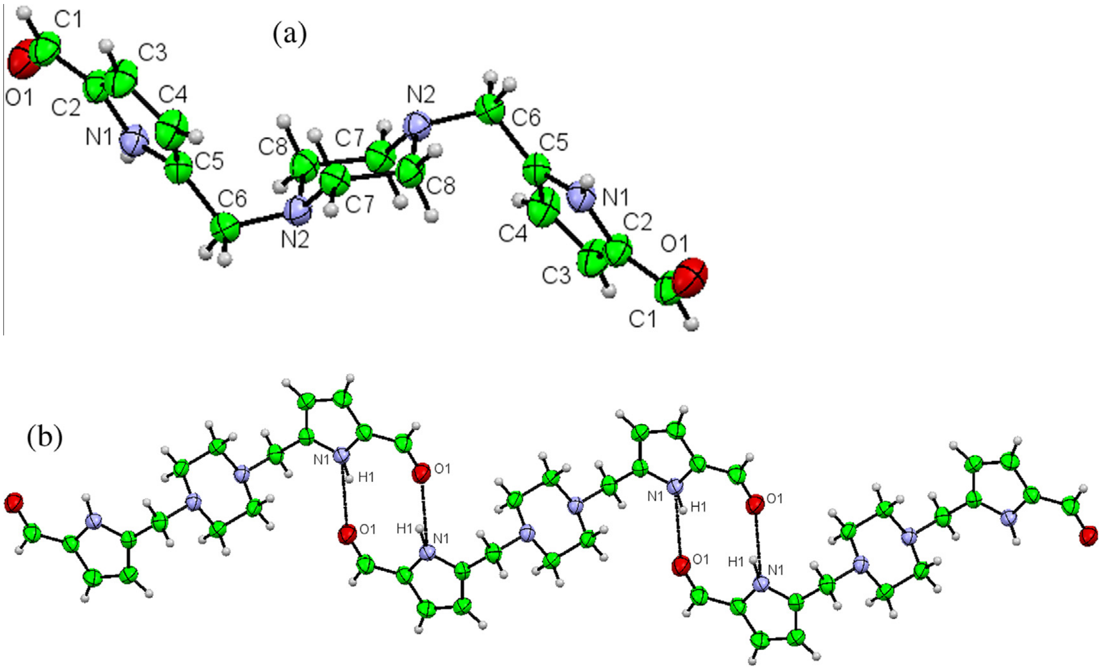


**Fig. 1.** The X-ray crystal structure of the *N*,*N*′-bis(5-formylpyrrol-2-ylmethyl)piperazine, **2**: (a) side view showing the e,e configuration/chair conformation and (b) the 1D supramolecular chain structure formed by the intermolecular H-bonds. Symmetry transformations used to generate equivalent atoms: (i) $-x$, $-y + 1$, $-z + 1$ and (ii) $-x - 1$, $-y + 1$, $-z$.

the cavity or solvent of crystallization in the lattice, which is a desirable property for metal complexation reactions that require moisture free conditions.

### *2.3. Synthesis and characterization of the binuclear copper(II) complexes*

The addition of one equiv of Schiff base **3** to a solution or suspension of two equiv of copper carboxylates $[Cu(OOCR)_2(H_2O)]$ (R = H, Me and Ph) in methanol results in an immediate color change to green, which afforded the dianionic form of the bis (iminopyrrolyl) ligand **3** bridged binuclear copper(II) complexes **6**, **7** and **8** in good crystalline yields (Scheme 3). These complexes contain two 'well-separated' copper atoms and are formed via cleavage of the carboxylate ion bridged binuclear copper complexes $[Cu(OOCR)_4(H_2O)_2]$, in which the two copper atoms lie closer, and deprotonation of the pyrrolic NH groups of ligand by the carboxylate anions, resulting in the formation of the corresponding carboxylic acids. The FT-IR spectra of these complexes show that the $\nu(C{=}N)$ stretching frequencies shifted to lower wave numbers as compared to that of the free ligand, indicating that the azomethine nitrogen is bound to the copper atom.

The structure of complexes **6**–**8**, given in Figs. 3–5, respectively, was determined by single crystal X-ray diffraction studies and their bond distances and angles are given in Table 1. It revealed that each copper atom is five-coordinate and the geometry around the copper atom is a distorted square pyramid with their axial bond distances (2.691(4) Å, 2.258(3) Å and 2.296(2) Å) being longer than the corresponding basal bond distances (1.944(4) Å, 2.013(3) Å and 1.997(2) Å) in **6**, **7** and **8**, respectively. However, these complexes differ by the constituent groups bonded to the copper atom. The acetate **7** and benzoate **8** complexes contain two methanol molecules: one in the basal and the other axial positions with the acetate and benzoate anions being coordinated in a monodentate $\kappa^1$-*O* fashion. Conversely, in the case of formate complex, one $H_2O$ is bonded in the basal plane; the axial position is occupied by one of the oxygen atoms of the anisobidentate chelating formate anion.

The Addison geometric parameters $\tau$ for each five-coordinate copper atom ($\tau = \beta - \alpha/60$, where $\beta$ and $\alpha$ are the two largest angles; $\tau_5 = 1$ for a trigonal bipyramid and $\tau_5 = 0$ for a square pyramidal structure) [14] are 0.18 (**6**), 0.38 (**7**) and 0.45 (**8**), indicating their distorted geometries; the distortion is more for **8** towards a trigonal bipyramid. Each complex contains two mean basal planes formed by the coordinated N and O donor atoms, which are parallel to each other owing to symmetry, and the distance between them is 1.703 Å for **6**, 2.453 Å for **7** and 1.220 Å for **8**. The copper atom is located 0.102 Å for the formate complex **6**, 0.282 Å for the acetate complex **7** and 0.304 Å for the benzoate complex **8** above the mean basal plane towards the apical donor atom. The Cu–N$_{\text{pyrrolide}}$ and the Cu–N$_{\text{imine}}$ bond distances range from 1.944(3) to 1.964(3) Å and 2.018(4) to 2.051(3) Å, respectively, which are closer to the values in copper complexes containing pyrrole-Schiff base ligands [1h,15]. The basal carboxylate Cu–O distances range from 1.923(2) to 2.013(3) Å which are also closer to the reported values [16].

In these structures, both inter- and intramolecular hydrogen bonding interactions are present and their metric parameters are given in Table 1. In the formate complex **6**, the two bound water molecules, one on each copper atom, form hydrogen bonds with the piperazine nitrogen atoms as hydrogen bond acceptors (Fig. 3). Besides, there are several intermolecular hydrogen bonds formed between the lattice MeOH molecules, coordinated water and carboxylate groups in the crystal lattice. In the case of acetate **7** (Fig. 4) and benzoate **8** (Fig. 5) complexes, as the structures contain four coordinated methanol molecules, each one forms one hydrogen bond with the adjacent hydrogen bond acceptors. While the apical methanol OH groups form hydrogen bonds with the spectator benzoate oxygen atoms, the basal methanol OH groups form the same with the piperazine nitrogen atoms. In total, the structure contains four intramolecular hydrogen bonds.

**Table 1**
Selected bond lengths (Å) and angles (°) for **2**, **3** and **6**–**8**.

| | | | |
|---|---|---|---|
| ***2*** | | | |
| C1–C2 | 1.422(2) | C2–N1–C5 | 109.88(14) |
| C2–N1 | 1.378(2) | C5–C6–N2 | 116.25(13) |
| N1–C5 | 1.352(2) | H1···O1 | 2.001(19) |
| C5–C6 | 1.499(2) | N1···O1 | 2.8660(19) |
| C6–N2 | 1.473(2) | N1–H1···O1 | 161.3(17) |
| C1–C2–N1 | 123.48(15) | | |
| ***3*** | | | |
| N1–C13 | 1.274(3) | C18–N3 | 1.458(3) |
| C13–C14 | 1.432(4) | N1–C13–C14 | 121.4(3) |
| C14–N2 | 1.377(3) | C14–N2–C17 | 110.5(2) |
| N2–C17 | 1.362(3) | C17–C18–N3 | 112.7(2) |
| C17–C18 | 1.488(4) | | |
| ***6*** | | | |
| N1–Cu1 | 2.018(4) | N1–Cu1–O1 | 93.72(16) |
| N2–Cu1 | 1.948(4) | N1–Cu1–N2 | 83.51(16) |
| Cu1–O1 | 1.944(4) | H2···N3 | 1.89(7) |
| Cu1–O2 | 2.691(4) | O3···N3 | 2.638(6) |
| Cu1–O3 | 1.928(4) | O3–H2···N3 | 163(7) |
| N1–Cu1–O3 | 159.70(17) | H5a···O4 | 1.92 |
| N2–Cu1–O1 | 170.82(15) | O5···O4 | 2.718(5) |
| O1–Cu1–O3 | 91.19(17) | O5–H5a···O4 | 163 |
| N2–Cu1–O3 | 94.40(17) | | |
| ***7*** | | | |
| N1–Cu1 | 2.051(3) | O(1)–Cu(1)–O(3) | 92.27(11) |
| N2–Cu1 | 1.964(3) | N(2)–Cu(1)–O(3) | 91.83(11) |
| Cu1–O1 | 1.944(2) | O(4)–Cu(1)–O(3) | 103.40(12) |
| Cu1–O3 | 2.258(3) | N(1)–Cu(1)–O(3) | 104.82(11) |
| Cu1–O4 | 2.013(3) | H1···O2 | 1.83(4) |
| O1–Cu1–N2 | 174.10(12) | O3···O2 | 2.592(4) |
| O(1)–Cu(1)–O(4) | 90.05(11) | O3–H1···O2 | 167(5) |
| N(2)–Cu(1)–O(4) | 93.13(12) | H2···N3 | 1.93(5) |
| O(1)–Cu(1)–N(1) | 92.42(11) | O4···N3 | 2.700(4) |
| N(2)–Cu(1)–N(1) | 82.42(12) | O4–H2···N3 | 173(5) |
| O(4)–Cu(1)–N(1) | 151.54(13) | | |
| ***8*** | | | |
| N1–Cu1 | 2.035(3) | N1–Cu1–O1 | 91.52(10) |
| N2–Cu1 | 1.944(3) | N1–Cu1–N2 | 82.85(11) |
| Cu1–O1 | 1.923(2) | O3–Cu1–O4 | 100.48(9) |
| Cu1–O3 | 1.997(2) | N1–Cu1–O4 | 111.66(10) |
| Cu1–O4 | 2.296(2) | H1···N3 | 1.99(4) |
| N1–Cu1–O3 | 147.44(10) | O3···N3 | 2.658(3) |
| N2–Cu1–O1 | 174.23(10) | O3–H1···N3 | 177(5) |
| O1–Cu1–O3 | 91.09(9) | H2···O2 | 1.79(4) |
| N2–Cu1–O3 | 93.00(10) | O4···O2 | 2.609(3) |
| | | O4–H2···O2 | 168(4) |

## 3. Conclusions

The regioselectivity, N versus α-C, of the Mannich reaction of pyrrole-2-carbaldehyde was explored with piperazine, giving two new dialdehyde molecules. The [1+2] Schiff base **3**, representing a new extended bis(iminopyrrolyl) ligand containing one piperazine ring, was synthesized in high yield. It readily afforded the three different 'well-separated' binuclear five-coordinate copper (II) complexes containing labile coordinated solvents. Their X-ray structures showed that both the piperazine nitrogens act as hydrogen bond acceptors, instead of coordination to the metal atom. Other metal complexation reactions including heterobimetallic complexes and catalytic properties will be our future research.

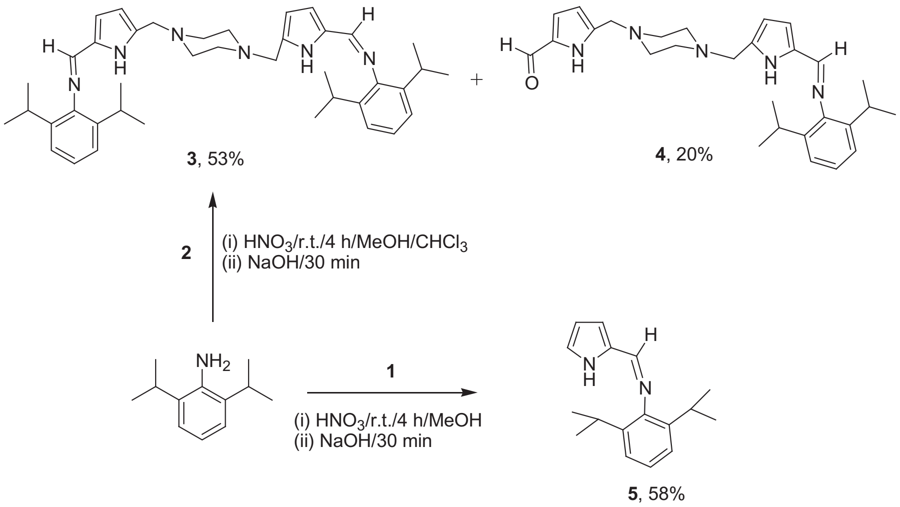
## 4. Experimental

### 4.1. General

All the reactions and manipulations were carried out in an open atmosphere or stated otherwise. Solvents were purchased from commercial sources and distilled prior to use by following standard procedures. Pyrrole-2-carbaldehyde was prepared as reported [17]. Pyrrole and $CDCl_3$ were used as received from Aldrich. Other chemicals were obtained from local commercial sources and were used without further purification. $^1H$ NMR (200 MHz), $^{13}C$ NMR (51.3 MHz) and Dept-135 NMR (51.3 MHz) spectra were recorded on Bruker spectrometers. Chemical shifts are referenced with respect to the chemical shift of the residual protons present in the deuterated solvents. FTIR spectra were recorded using Perkin Elmer Spectrum Rx. High Resolution Mass Spectra (ESI) were recorded using LCT Orthogonal Acceleration TOF Electrospray Mass Spectrometer. Elemental analyses were carried out using a Perkin–Elmer 2400 CHN analyzer. UV–Vis spectra were recorded on SHIMADZU UV-2450 spectrophotometer. Melting points were determined in open capillaries and are corrected using benzophenone as a reference.

### 4.2. Synthesis of N,N′-bis(5-formylpyrrol-1-ylmethyl)piperazine *1*

To a suspension of piperazine (0.43 g, 5.00 mmol) and formaldehyde (38%, 0.80 mL, 10.00 mmol) in methanol/water (20 ml, v/v 2:1) was added a solution of pyrrole-2-carbaldehyde



**Scheme 2.** The Schiff base condensation reactions for the dialdehydes **1** and **2**: synthesis of the bis(iminopyrrolyl) **3** and monoiminopyrrolyl **4** ligands containing the piperazine ring.

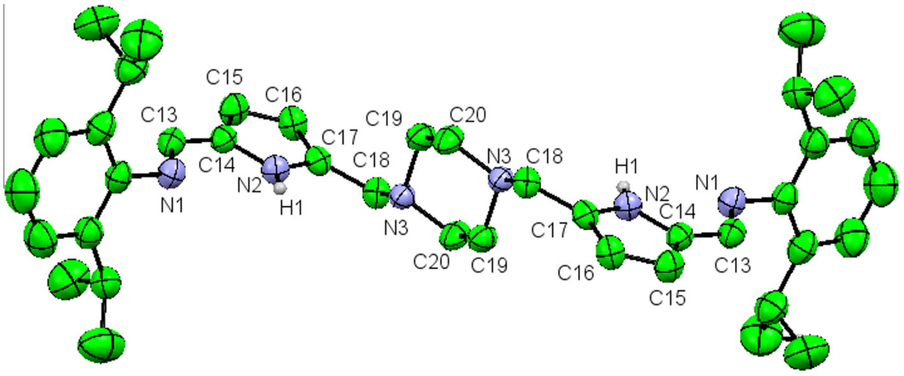
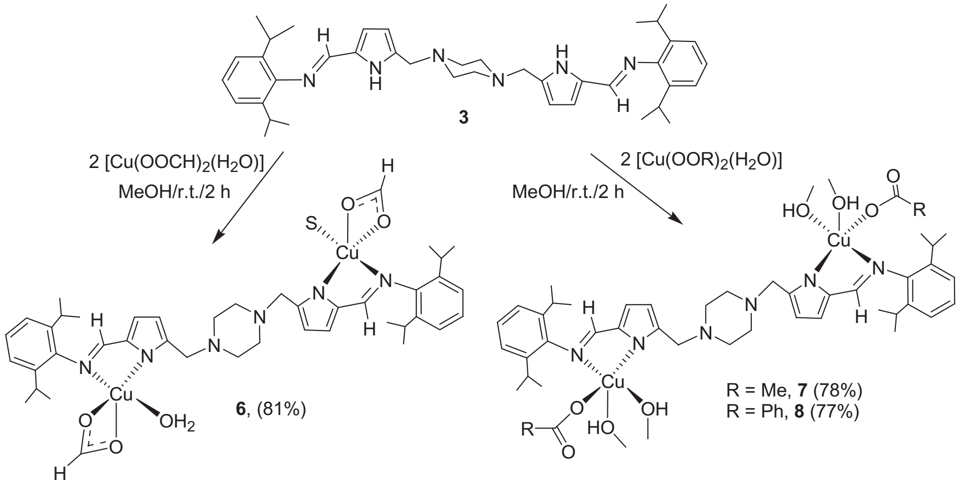


**Fig. 2.** The X-ray crystal structure of the Schiff base **3**. Symmetry transformations used to generate equivalent atoms: −*x* + 1, −*y* + 1, −*z*.



**Scheme 3.** Synthesis of the binuclear copper(II) complex **6**–**8** containing the bis(iminopyrrolyl) ligand **3**.

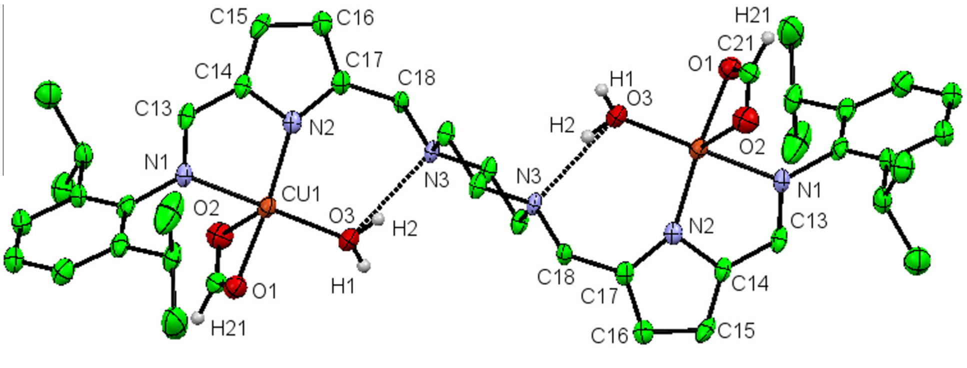


**Fig. 3.** The X-ray crystal structure of the dinuclear Cu(II) formate complex **6**. Most H atoms and lattice MeOH are omitted for clarity. Dotted lines indicate hydrogen bonding. Symmetry transformations used to generate equivalent atoms: (i) −*x* + 1, −*y* + 1, −*z* + 1, (ii) −*x* + 1, −*y* + 1, −*z* and (iii) −*x*, −*y* + 1, −*z*.

(0.95 g, 10.00 mmol) in methanol (5 mL) and the solution was stirred overnight (15 h) at room temperature. The solvent was removed under vacuum and the resulting residue was extracted with chloroform (2 × 15 mL). The chloroform solution was dried over anhydrous sodium sulfate for two hours and then filtered. The solvent was removed under vacuum to give compound **1** as oily residue which became solid over a period of three hours (1.06 g, 3.53 mmol, 71%). mp 96 °C. $^1$H NMR (200 MHz, $CDCl_3$, 25 °C, ppm): $\delta$ = 2.56 (s, 8H, $N(CH_2)_4N$), 5.15 (s, 4H, $CH_2N(CH_2)_4NCH_2$), 6.23 (m, 2H, pyrrole β-C*H*), 6.97–6.92 (m, 4H, pyrrole β-C*H* and pyrrole α-C*H*), 9.52 (s, 2H, C*H*O). $^{13}C\{^1H\}$NMR (51.3 MHz, $CDCl_3$, 25 °C, ppm): $\delta$ = 49.9 ($N(CH_2)_4N$), 68.8 ($CH_2N(CH_2)_4NCH_2$), 109.9 (pyrrole β-*C*), 125.4 (pyrrole β-*C*), 132.1 (pyrrole α-*C*), 132.5 (pyrrole α-*C*), 179.9 (*C*HO). DEPT-135$\{^1H\}$NMR (51.3 MHz, $CDCl_3$, 25 °C, ppm): $\delta$ = 49.7 ($N(CH_2)_4N$), 68.6 ($CH_2N(CH_2)_4NCH_2$), 109.7 (pyrrole β-*C*), 125.2 (pyrrole β-*C*), 131.9 (pyrrole α-*C*), 179.8 (*C*HO). FT-IR (KBr, cm$^{-1}$): $\nu$ = 3296 (w), 3104 (w), 2948 (w), 2917 (w), 2884 (w), 2835 (m), 2717 (w), 1657 (vs), 1525 (w), 1473 (m), 1455 (m), 1422 (w), 1403 (vs), 1372 (s), 1353 (s), 1328 (m), 1287 (s), 1209 (w), 1164 (vs), 1133 (m), 1079 (s), 1067 (m),

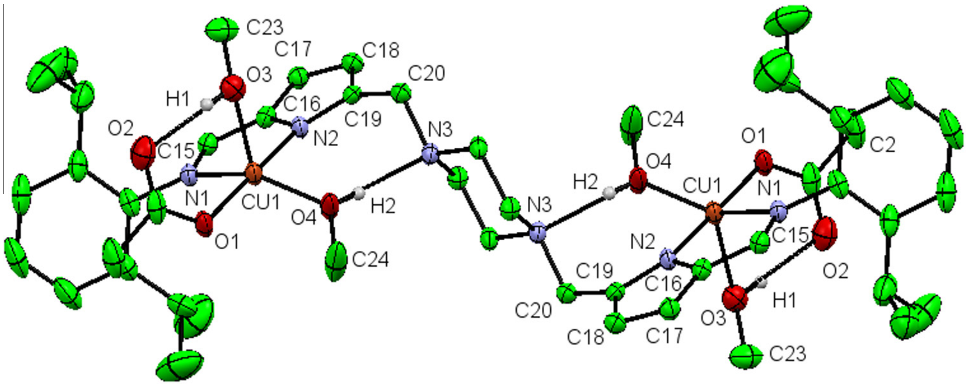


**Fig. 4.** The X-ray crystal structure of the dinuclear Cu(II) acetate complex **7**. Most H atoms are omitted for clarity. Dotted lines indicate hydrogen bonding. Symmetry transformations used to generate equivalent atoms: (i) $-x + 1$, $-y$, $-z + 1$ and (ii) $-x + 1$, $y + 1/2$, $-z + 1/2$.

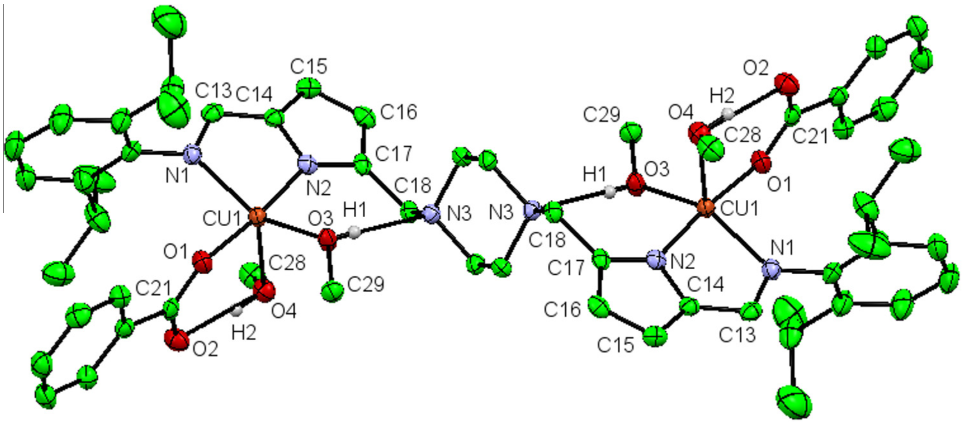


**Fig. 5.** The X-ray crystal structure of the dinuclear Cu(II) benzoate complex **8**. Most H atoms and lattice MeOH are omitted for clarity. Dotted lines indicate hydrogen bonding. Symmetry transformations used to generate equivalent atoms: (i) $-x + 1$, $-y$, $-z + 1$ and (ii) $-x + 3/2$, $-y + 3/2$, $z$.

1036 (m), 1011 (s), 881 (w), 793 (w), 767 (vs), 747 (vs), 650 (m), 609 (m), 497 (w). HRMS(+ESI): calc. $m/z$ for $[M+H^+]$ $C_{16}H_{21}N_4O_2$: 301.1665, found: 301.1626.

### 4.3. Synthesis of N,N′-bis(5-formylpyrrol-2-ylmethyl)piperazine, **2**

To a suspension of piperazine (0.43 g, 5.00 mmol) and formaldehyde (38%, 0.80 mL, 10.00 mmol) in methanol/water (20 mL, $v/v$ 2:1) was added conc. HCl (12 N, 0.83 mL, 10.00 mmol) at room temperature. The reaction mixture turned to a homogeneous solution. A solution of pyrrole-2-carbaldehyde (0.95 g, 10.00 mmol) in methanol (5 mL) was added and the solution was stirred overnight (15 h) to give colorless precipitate. Solid NaOH (0.40 g, 10.00 mmol) was then added and the resulting reaction mixture was stirred for one hour. Methanol was partially removed under vacuum and the reaction mixture was filtered. The precipitate was washed with water ($2 \times 5$ mL) and dried under vacuum to give **2** (1.06 g, 3.53 mmol, 71%) as colorless solid. mp > 200 °C. $^1H$ NMR (200 MHz, $CDCl_3$, 25 °C, ppm): $\delta = 2.50$ (s, 8H, $N(CH_2)_4N$), 3.56 (s, 4H, $CH_2N(CH_2)_4NCH_2$), 6.16 (t, 2H, $^3J(H,H) = 4$ Hz, pyrrole β-CH), 6.89 (t, 2H, $^3J(H,H) = 4$ Hz, pyrrole β-CH), 9.43 (s, 2H, CHO), 9.61 (br s, 2H, NH). $^{13}C\{^1H\}$ NMR (51.3 MHz, $CDCl_3$, 25 °C, ppm): $\delta = 53.3$ ($N(CH_2)_4N$), 55.2 ($CH_2N(CH_2)_4NCH_2$), 110.6 (pyrrole β-C), 121.9 (pyrrole β-C), 132.7 (pyrrole α-C), 138.2 (pyrrole α-C), 178.9 (CHO). DEPT-135$\{^1H\}$ NMR (51.3 MHz, $CDCl_3$, 25 °C, ppm): $\delta = 53.0$ ($N(CH_2)_4N$), 54.9 ($CH_2N(CH_2)_4NCH_2$), 110.4 (pyrrole β-C), 121.7 (pyrrole β-C), 178.6 (CHO). FT-IR (KBr, $cm^{-1}$): $\nu = 3239$ (s), 2940 (w), 2826 (m), 1642 (vs), 1560 (w), 1490 (m), 1460 (w), 1416 (m), 1359 (w), 1339 (m), 1273 (w), 1190 (s), 1141 (w), 1055 (m), 1013 (w), 886 (w), 818 (m), 766 (m), 642 (w), 424 (w). HRMS(+ESI): calc. $m/z$ for $[M+H^+]$ $C_{16}H_{21}N_4O_2$: 301.1665, found: 301.1626.

### 4.4. Synthesis of bis(iminopyrrolyl), **3** and monoiminopyrrolyl, **4** ligands

To a solution of **2** (0.92 g, 3.06 mmol) and 2,6-diisopropylaniline (1.21 mL, 6.41 mmol) in methanol/chloroform (30 mL, $v/v$ 2:3) was added conc. $HNO_3$ (16 N, 0.40 mL, 6.41 mmol), resulting in an immediate formation of colorless precipitate. The solution was stirred for 4 h at room temperature. Solid NaOH (0.26 g, 6.41 mmol) was then added and stirred for an additional 0.5 h. The solvent was removed under vacuum and the resulting residue was extracted with dichloromethane which was loaded onto a column chromatography filled with silica gel. Elution using ethyl acetate/petroleum ether ($v/v$ 1:2) afforded the first fraction from which the solvents were removed under vacuum to give Schiff base **3** (1.01 g, 1.63 mmol, 53%) as colorless solid. Further elution using the same solvent mixture yielded the second fraction from which the solvents were removed under vacuum to give the mono Schiff base **4** (0.280 g, 0.61 mmol, 20%) as colorless solid.

For **3**: mp 166 °C. $^1H$ NMR (200 MHz, $CDCl_3$, 25 °C, ppm): $\delta = 1.17$ (d, 24H, $^3J(H,H) = 7$ Hz, $CH_3$), 2.65 (s, 8H, $N(CH_2)_4N$), 2.97–3.11 (m, 2H, CH), 3.65 (s, 4H, $CH_2–N(CH_2)_4N–CH_2$), 6.18 (d, 2H, $^3J(H,H) = 3.4$ Hz, pyrrole β-CH), 6.55 (d, 2H, $^3J(H,H) = 3.2$ Hz, pyrrole β-CH), 7.13–7.16 (m, 6H, benzene CH), 7.85 (s, 2H, H*C* = N). $^{13}C\{^1H\}$ NMR (51.3 MHz, $CDCl_3$, 25 °C, ppm): $\delta = 23.9$ ($CH_3$), 28.0 (*C*H), 53.3 ($N(CH_2)_4N$), 55.5 ($CH_2–N(CH_2)_4N–CH_2$), 109.9 (pyrrole β-*C*), 116.3 (pyrrole β-*C*), 123.2 (benzene-*C*), 124.2 (benzene-*C*), 130.2 (pyrrole α-*C*), 134.5 (pyrrole α-*C*), 138.6 (benzene-*C*), 149.0 (benzene-*C*), 151.8 (H*C*=N). DEPT-135$\{^1H\}$ NMR (51.3 MHz, $CDCl_3$, 25 °C, ppm): $\delta = 23.9$ ($CH_3$), 28.0 (*C*H), 53.3 ($N(CH_2)_4N$), 55.5 ($CH_2–N(CH_2)_4N–CH_2$), 109.8 (pyrrole β-*C*), 116.3 (pyrrole β-*C*), 123.2 (benzene-*C*), 124.2 (benzene-*C*), 151.7 (H*C*=N). FT-IR (KBr, $cm^{-1}$): $\nu = 3446$ (m), 2958 (m), 2923 (w), 2821 (w), 2364 (w), 1720 (w), 1627 (s), 1588 (w), 1562 (w), 1499 (w), 1458 (w), 1437 (w), 1385 (w), 1335 (w), 1294 (w), 1232 (w), 1159 (m), 1134 (w), 1051 (w), 1009 (w), 930 (w), 857 (w), 830 (w), 793 (m), 749 (w), 718 (w), 677 (w), 578 (w). HRMS(+ESI): calc. *m/z* for $[M+H^+]$ $C_{40}H_{55}N_6$: 619.4488, found: 619.4512.

For **4**: mp 174 °C. $^1H$ NMR (200 MHz, $CDCl_3$, 25 °C, ppm): $\delta = 1.17$ (d, 12H, $^3J(H,H) = 6.8$ Hz, $CH_3$), 2.60 (s, 8H, $N(CH_2)_4N$), 2.96–3.10 (m, 2H, C*H*), 3.60 (s, 2H, $CH_2N(CH_2)_4NCH_2$), 3.64 (s, 2H, $CH_2N(CH_2)_4NCH_2$), 6.17 (d, 2H, $^3J(H,H) = 3.2$ Hz, pyrrole β-C*H*), 6.57 (d, 1H, $^3J(H,H) = 3.2$ Hz, pyrrole β-C*H*), 6.88 (d, 1H, $^3J(H,H) = 3.6$ Hz, pyrrole β-C*H*), 7.02–7.18 (m, 3H, benzene C*H*), 7.84 (s, 1H, *H*C=N), 9.44 (s, 1H, C*H*O), 9.82 (br s, 1H, N*H*). $^{13}C\{^1H\}$ NMR (51.3 MHz, $CDCl_3$, 25 °C, ppm): $\delta = 23.9$ ($CH_3$), 28.1 (*C*H), 53.0 ($N(CH_2)_4N$), 55.0 ($CH_2N(CH_2)_4NCH_2$), 110.4 (pyrrole β-*C*), 110.8 (pyrrole β-*C*), 121.8 (pyrrole β-*C*), 123.3 (benzene-*C*), 124.6 (pyrrole β-*C*), 132.8 (pyrrole α-*C*), 139.0 (pyrrole α-*C*), 151.9 (H*C*=N), 178.9 (*C*HO). DEPT-135$\{^1H\}$ NMR (51.3 MHz, $CDCl_3$, 25 °C, ppm): $\delta = 23.7$ ($CH_3$), 27.9 (*C*H), 52.8 ($N(CH_2)_4N$), 55.1 ($CH_2–N(CH_2)_4N–CH_2$), 110.2 (pyrrole β-*C*), 110.6 (pyrrole β-*C*), 121.7 (pyrrole β-*C*), 123.1 (benzene-*C*), 124.5 (pyrrole β-*C*), 151.8 (H*C*=N), 178.7 (*C*HO). FT-IR (KBr, $cm^{-1}$): $\nu = 3255$ (m), 2957 (m), 2813 (w), 1634 (s), 1439 (m), 1342 (m), 1169 (m), 1040 (m), 784 (m). HRMS (+ESI): calc. *m/z* for $[M+H^+]$ $C_{28}H_{38}N_5O_1$: 460.3076, found: 460.3111.

### 4.5. Synthesis of iminopyrrole **5**

To a solution of **1** (0.205 g, 0.68 mmol) and 2,6-diisopropylaniline (0.26 mL, 1.37 mmol) in methanol/chloroform (30 mL, *v/v* 2:3) was added conc. $HNO_3$ (16 N, 0.085 mL, 1.37 mmol), giving a clear solution. After stirring the solution for 21 h at room temperature, solid NaOH (0.055 g, 1.37 mmol) was added and stirring continued for an additional 0.5 h. The solvent was removed under vacuum and the resulting residue was extracted with dichloromethane, which was loaded onto a column chromatography filled with silica gel. Elution using ethyl acetate/petroleum ether (*v/v* 1:5) afforded the first fraction from which the solvents were removed under vacuum to give Schiff base **5** (0.20 g, 0.79 mmol, 58%) as colorless solid. The structure of **5** is confirmed by matching the $^1H$ and $^{13}C$ NMR spectra with the reported ones.

### 4.6. Synthesis of the binuclear copper(II) formate complex, **6**

To a solution of $[Cu(OOCH)_2(H_2O)]$ (0.035 g, 0.2 mmol) in methanol (10 mL) was added solid **3** (0.062 g, 0.1 mmol) and the color of the solution immediately changed to green. The solution was stirred at room temperature for 2 h, giving a little amount of precipitation. Dichloromethane (10 mL) was then added and the solution became a homogeneous solution, which yielded dark green crystals of **6** upon slow evaporation of the solvents at room temperature. These crystals become amorphous immediately in the absence of mother liquor. Yield: 0.071 g, 0.081 mmol, 81% without 4MeOH solvents of crystallization). Mp > 200 °C. FT-IR (KBr, $cm^{-1}$): $\nu = 2961$ (s), 2868 (m), 2832 (m), 1609 (vs), 1570 (vs), 1502 (w), 1476 (m), 1459 (m), 1418 (w), 1379 (m), 1347 (m), 1305 (m), 1284 (s), 1258 (m), 1176 (m), 1116 (w), 1055 (s), 990 (w), 933 (w), 895 (w), 825 (w), 778 (m), 761 (m), 734 (w), 674 (w), 571 (w), 451 (w). *Anal.* Calc. for $C_{42}H_{58}N_6O_6Cu_2$: C, 57.98; H, 6.72; N, 9.66. Found: C, 57.61; H, 6.87; N, 9.86%.

### 4.7. Synthesis of the binuclear copper(II) acetate complex, **7**

To a solution of $[Cu(OAc)_2(H_2O)]$ (0.040 g, 0.2 mmol) in methanol (8 mL) was added solid **3** (0.062 g, 0.1 mmol) and the color of the solution immediately changed to green. The solution was stirred at room temperature for 2 h, giving a little amount of precipitation. Dichloromethane (3 mL) was then added and the solution became a homogeneous solution, which yielded dark green crystals of **7** upon slow evaporation of the solvents at room temperature. Yield: 0.072 g, 0.075 mmol, 75% based on **7**·$2H_2O$. Mp 168 °C. FT-IR (KBr, $cm^{-1}$): $\nu = 3434$ (w), 2962 (m), 1578 (vs), 1431 (m), 1384 (m), 1308 (m), 1286 (m), 1260 (w), 1178 (w), 1052 (m), 992 (w), 933 (w), 894 (w), 825 (w), 757 (w), 732 (w), 674 (w), 617 (w). *Anal.* Calc. for $C_{46}H_{70}N_6O_8Cu_2$: C, 57.42; H, 7.33; N, 8.73. Found: C, 57.97; H, 7.91; N, 8.90%.

### 4.8. Synthesis of the binuclear copper(II) benzoate complex, **8**

To a suspension of $[Cu(OOCPh)_2(H_2O)]$ (0.065 g, 0.2 mmol) in methanol (10 mL) was added solid **3** (0.062 g, 0.1 mmol) and the color of the solution immediately changed to green. The solution was stirred at room temperature for 2 h, resulting in the precipitate formation. Dichloromethane (10 mL) was then added and the solution became a homogeneous solution, which yielded dark green crystals of **8** upon slow evaporation of the solvents at room temperature. Yield: 0.089 g, 0.077 mmol, 77% based on **8**·MeOH. Mp 174 °C. FT-IR (KBr, $cm^{-1}$): $\nu = 3063$ (w), 2961 (s), 2868 (m), 2826 (w), 1597 (vs), 1575 (vs), 1460 (m), 1446 (m), 1377 (vs), 1307 (s), 1283 (s), 1257 (m), 1176 (m), 1139 (w), 1054 (vs), 1025 (w), 991 (w), 933 (w), 895 (w), 823 (w), 805 (w), 758 (m), 718 (s), 681 (m), 572 (w), 456 (w). *Anal.* Calc. for $C_{58}H_{78}N_6O_8Cu_2$: C, 62.51; H, 7.06; N, 7.54. Found: C, 62.32; H, 7.04; N, 7.98%.

### 4.9. X-ray crystallography

Suitable single crystals of **2** and **3** for X-ray diffraction studies were obtained by slow evaporation of a solution of **2** and **3** in petroleum ether/dichloromethane (1:1 *v/v*). Similarly, the slow evaporation of a solution of **6**–**8** in methanol/dichloromethane (2:1 *v/v*) gave suitable single crystals of **6**–**8**.

Single crystal X-ray diffraction data collections for all the compounds were performed using Bruker-APEX-II CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The space group for every structure was obtained by XPREP program. The structures were then solved by SIR-92 [18] or SHELXS-97 [19] available in WinGX, which successfully located most of the non-hydrogen atoms. Subsequently, least square refinements were carried out on $F^2$ using SHELXL-97 (WinGX version) to locate the remaining non-hydrogen atoms. Non-hydrogen atoms were refined with anisotropic displacement parameters. The pyrrolic NH, methanol OH and water hydrogens were located from the difference Fourier maps; all other hydrogen atoms were placed at calculated positions and refined using a riding model with fixed isotropic displacement parameters that were 1.2–1.5 times the equivalent isotropic displacement parameter for the parent atom to which a given hydrogen atom was bonded. The formate complex **6** crystallizes in the centrosymmetric triclinic space group $P\bar{1}$. The asymmetric unit consists of one half of the molecule and two MeOH molecules. The acetate complex **7** crystallizes in the centrosymmetric monoclinic space group $P2_1/c$. The asymmetric unit contains one half of the molecule. The structure of the benzoate complex **8** was solved in the centrosymmetric orthorhombic *Pccn*

**Table 2**
Crystal data and structure refinement for **2**, **3** and **6**–**8**.

| | **2** | **3** | **6**·4MeOH | **7** | **8**·MeOH |
|---|---|---|---|---|---|
| Empirical formula | $C_{16}H_{20}N_4O_2$ | $C_{40}H_{54}N_6$ | $C_{46}H_{74}Cu_2N_6O_{10}$ | $C_{48}H_{74}Cu_2N_6O_8$ | $C_{59}H_{82}Cu_2N_6O_9$ |
| Formula weight | 300.36 | 618.89 | 998.19 | 990.21 | 1146.38 |
| Wavelength (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| $T$ (K) | 293(2) | 293(2) | 100(2) | 100(2) | 100(2) |
| Crystal system | triclinic | triclinic | triclinic | monoclinic | orthorhombic |
| Color and shape | colorless | colorless | green | green | green |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P2_1/c$ | $Pccn$ |
| $a$ (Å) | 5.3756(6) | 6.381(3) | 9.270(3) | 16.647(3) | 35.432(3) |
| $b$ (Å) | 7.7191(9) | 7.405(4) | 11.152(4) | 9.6898(19) | 10.9934(10) |
| $c$ (Å) | 10.2528(16) | 20.224(10) | 13.282(5) | 16.057(3) | 14.9308(13) |
| $\alpha$ (°) | 107.841(4) | 99.299(16) | 77.375(11) | 90 | 90 |
| $\beta$ (°) | 92.989(4) | 95.148(16) | 75.184(11) | 94.725(6) | 90 |
| $\gamma$ (°) | 109.053(3) | 100.748(16) | 77.569(12) | 90 | 90 |
| $V$ (Å$^3$) | 377.28(8) | 919.3(8) | 1276.7(8) | 2581.3(9) | 5815.8(9) |
| $Z$ | 1 | 1 | 1 | 2 | 4 |
| $D_{calc}$ (g cm$^{-3}$) | 1.322 | 1.118 | 1.298 | 1.274 | 1.309 |
| $\mu$ (mm$^{-1}$) | 0.090 | 0.066 | 0.891 | 0.878 | 0.791 |
| $F(000)$ | 160 | 336 | 530 | 1052 | 2432 |
| $\theta$ range (°) | 2.117–24.996 | 1.028–24.994 | 1.610–25.000 | 2.434–24.999 | 1.149–24.962 |
| Limiting indices | $-6 \leqslant h \leqslant 6$, $-9 \leqslant k \leqslant 9$,<br>$-12 \leqslant l \leqslant 12$ | $-7 \leqslant h \leqslant 7$, $-8 \leqslant k \leqslant 8$,<br>$-23 \leqslant l \leqslant 23$ | $-11 \leqslant h \leqslant 11$,<br>$-13 \leqslant k \leqslant 10$,<br>$-15 \leqslant l \leqslant 14$ | $-19 \leqslant h \leqslant 19$,<br>$-10 \leqslant k \leqslant 11$,<br>$-19 \leqslant l \leqslant 19$ | $-42 \leqslant h \leqslant 42$,<br>$-13 \leqslant k \leqslant 13$,<br>$-17 \leqslant l \leqslant 15$ |
| Total/unique no. of reflns. | 4387/1320 | 10937/3209 | 13220/4292 | 28643/4515 | 64863/5084 |
| $R_{int}$ | 0.0214 | 0.0732 | 0.0623 | 0.1033 | 0.0877 |
| Data/restr./params. | 1320/0/103 | 3209/0/211 | 4292/0/299 | 4515/0/295 | 5084/0/355 |
| Goodness-of-fit (GOF) on $F^2$ | 1.081 | 1.004 | 1.116 | 1.085 | 1.007 |
| $R_1$, $wR_2$ | 0.0387, 0.1023 | 0.0569, 0.1277 | 0.0586, 0.1666 | 0.0479, 0.1185 | 0.0465, 0.1288 |
| $R$ indices (all data) $R_1$, $wR_2$ | 0.0468, 0.1076 | 0.1328, 0.1740 | 0.0869, 0.2049 | 0.0769, 0.1349 | 0.0642, 0.1450 |
| Largest different peak and hole (e Å$^{-3}$) | 0.137 and −0.227 | 0.207 and −0.265 | 0.761 and −1.018 | 0.424 and − 0.653 | 1.011 and −0.537 |

space group. The asymmetric unit contains one half of the molecule and one disordered methanol at the special position as solvent of crystallization. Methanol hydrogens could not be placed at calculated positions or located and refined. The refinement data for all the structures are summarized in Table 2.

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## Appendix A. Supplementary material

CCDC 1418676–1418678, 1418680 and 1440314 contains the supplementary crystallographic data for **2**, **3** and **6–8**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2016.02.023.

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