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Dinuclear copper(II) complexes based on two multidentate flexible Schiff-base ligands and one unusual *in situ* formed diphenolate 2,6-piperidin-4-one derivative

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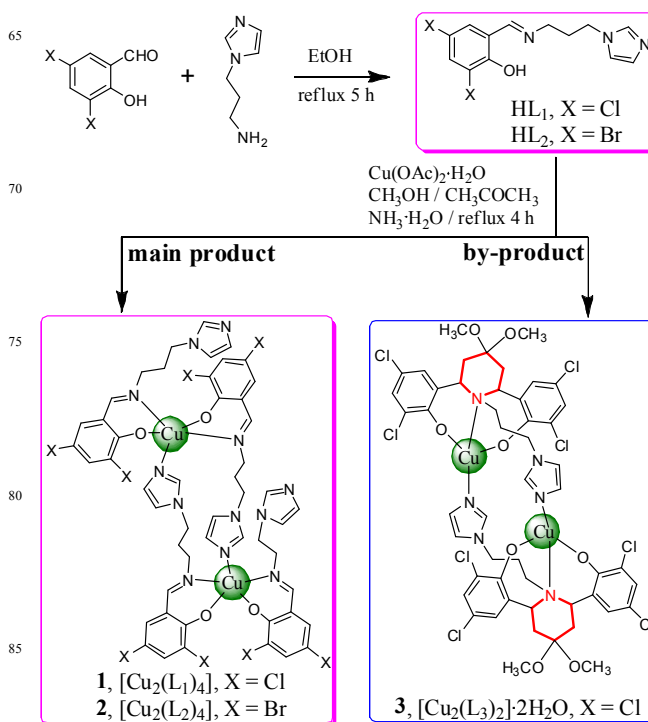
A dinuclear Cu(II) complex $[\text{Cu}_2(\text{L}_3)_2] \cdot 2\text{H}_2\text{O}$, having an unprecedented *in situ* formed diphenolate 2,6-piperidin-4-one derived ligand produced from the flexible Schiff-base ligand HL_1 , can be yielded as a side product in the presence of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O} / \text{NH}_3 \cdot \text{H}_2\text{O}$ dissolved in methanol and acetone, besides the expected dinuclear Cu(II) complex $[\text{Cu}_2(\text{L}_1)_4]$.

Schiff bases are a vital kind of ligands, and they can be facilely synthesized and coordinated with a variety of metal ions. The construction of transition-metal complexes having Schiff-base ligands has become one of the hottest research topics in modern coordination chemistry. Recent researches show that Schiff-base complexes have various applications such as anticancer agents,^{1–3} homogeneous or heterogeneous catalysis,^{4,5} ionic liquids,^{6–9} photochromism.^{10–15} Among them, some Schiff-base ligands, derived from the reversible condensation between salicylaldehyde derivatives and flexible amines, and their Cu(II) complexes have been investigated in literature.^{16–18} The construction of Schiff-base complexes can be regarded as metal-assisted self-assembly, which is commonly reported in literatures.¹⁹

In our previous work, a series of Schiff-base macrocyclic metal complexes bearing salicylaldehyde-based components have been studied.²⁰ In addition, a Schiff-base ligand obtained from the condensation between salicylaldehyde and *N*-(3-aminopropyl)imidazole, exhibiting multi-farious coordination fashions with copper(II) and cadmium(II), has been investigated.²¹ As a further study of this work, we report herein the syntheses and structural characterizations of two new flexible Schiff-base ligands HL_1 and HL_2 , derived from the condensation between dihalogen substituted salicylaldehyde and *N*-(3-aminopropyl)imidazole, and their dinuclear five-coordinate Cu(II) complexes formulated as $[\text{Cu}_2(\text{L}_1)_4]$ (**1**) and $[\text{Cu}_2(\text{L}_2)_4]$ (**2**), respectively, in which two of the L_1 and L_2 ligands are tridentate and the other two are bidentate. Furthermore, a unique tetradentate divalent anionic ligand L_3 including an *in situ* formed piperidine ring is obtained, which is suggested to come from the monovalent anionic ligand L_1 . As a result, another dinuclear Cu(II) complex **3** with the formula of $[\text{Cu}_2(\text{L}_3)_2] \cdot 2\text{H}_2\text{O}$ has been produced where the Schiff-base C=N unit in ligand L_1 disappears.

As shown in Scheme 1, two flexible Schiff-base ligands HL_1 and HL_2 were prepared in high yields by the condensation reaction between *N*-(3-aminopropyl)imidazole and 3,5-dichlorosalicylaldehyde/3,5-dibromosalicylaldehyde, where several drops of glacial acetic acid was added as a catalyst to promote the reaction. Complex **1** was synthesized using $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ as

metal source in the acetone/methanol mixture with excess aqueous ammonia. The microcrystals of complex **1** (main product) and complex **3** (by-product) were obtained simultaneously in the same beaker by slow evaporation in air at room temperature for two weeks. Control experiments by altering the reflux time for 1, 2, 4 and 8 hours indicate that the yield of complex **3** could be gradually increased with the reaction proceeding, and it reaches the maximum of 23% after 4h reflux with crystal formation after slow evaporation of solvent after two weeks. The synthesis of complex **2** was similar to that described for complex **1**.²² Nevertheless, the yield for ring formation reaction of L_2 is much lower since the required brown crystals corresponding to **3** are present in a very small amount (unsuitable for X-ray diffraction) among green crystals of **2** and it is very difficult to be isolated and characterized.



Scheme 1 Schematic illustration for the preparation of three dinuclear Cu(II) complexes.

In the FT-IR spectra of HL_1 and HL_2 (Fig. S11 and Fig. S12), a strong absorption peak is observed for each at 1632 and 1641 cm^{-1} , indicating the formation of the Schiff-base C=N unit. In

contract, such a band is shifted to 1623 cm^{-1} in complexes **1** and **2** (Fig. SI3 and Fig. SI4), reflecting the influence of metal-ion complexation on the coordinated C=N unit. However, such a strong peak cannot be found in the FT-IR spectrum of complex **3** (Fig. SI5), suggesting the disappearance of C=N moiety of *in situ* formed ligand L_3 after metal-ion complexation. In addition, negative ESI-MS spectra of HL_1 and HL_2 clearly show the presence of a molecular ion peak with 100% ion abundance (Fig. SI6 and Fig. SI7). However, it is difficult for us to obtain high quality ESI-MS spectra of all three dinuclear Cu(II) complexes.

UV-Vis absorption spectra of complexes **1–3** have been compared with those of corresponding ligands HL_1 and HL_2 , as can be seen in Fig. SI12, where DMF was used to record the UV-Vis absorption spectrum of complex **3** because of its poor solubility in methanol. The electronic spectra of two ligands are very similar having two absorption bands centered at 295 and 372 nm for HL_1 and 291 and 375 nm for HL_2 , respectively. The former for each is assigned as the $\pi\text{-}\pi^*$ electronic transition of the phenolic ring, while the latter is attributed to the $\pi\text{-}\pi^*$ charge transition of the azomethine chromophore. After copper(II) ion complexation, UV-Vis absorption spectra of complexes **1** and **2** are also nearly identical, where a new $d\text{-}d$ transition absorption peak emerges at 423 and 425 nm for each. In comparison with **1** and **2**, the broad $d\text{-}d$ transition absorption peak of **3** is slightly red-shifted to 428 nm. Furthermore, the phase purity of dinuclear Cu(II) complexes **1–3** has been confirmed by the PXRD patterns (Fig. SI13–Fig. SI15), in which the simulated and as-synthesized spectra are almost the same.

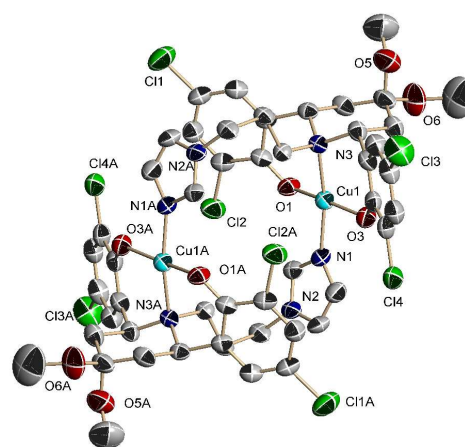
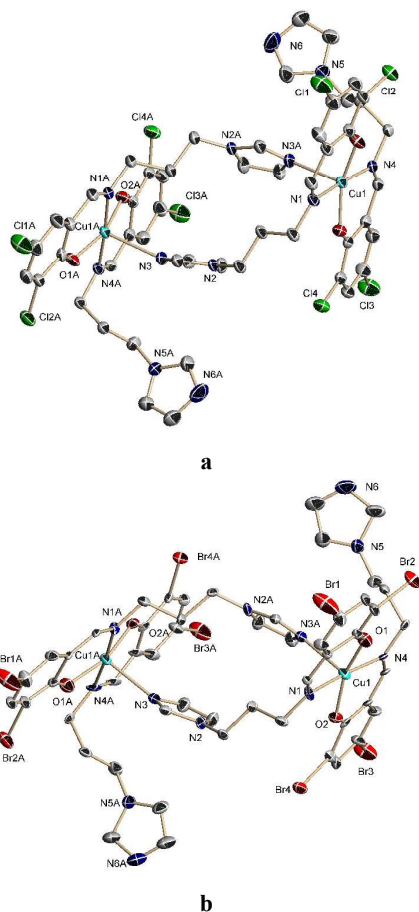


Fig. 1 ORTEP diagrams (30% thermal probability level ellipsoids) of the molecular structures of three dinuclear Cu(II) complexes **1** (a), **2** (b) and **3** (c) with the atom-numbering scheme. Selected bond lengths (Å): **1**: Cu1–O1, 1.920(3), Cu1–O2, 1.919(2), Cu1–N1, 2.035(3), Cu1–N4, 2.038(3), Cu1–N3A, 2.381(3), C7–N1, 1.278(5), C8–N1, 1.479(4). **2**: Cu1–O1, 1.893(14), Cu1–O2, 1.914(11), Cu1–N1, 2.021(12), Cu1–N4, 2.007(14), Cu1–N3A, 2.302(15). **3**: Cu1–O1, 1.883(4), Cu1–O3, 1.897(4), Cu1–N1, 1.973(5), Cu1–N3, 2.041(4), C7–N3, 1.498(6), C14–N3, 1.524(6), C20–N3, 1.485(6). Symmetry code: $1-x, y, 3/2-z$.

ORTEP diagrams with the numbering schemes of the molecular structures of three dinuclear Cu(II) complexes are given in Fig. 1.²³ X-ray single-crystal diffraction studies for **1** and **2** reveal that each Cu(II) ion is five-coordinated by three nitrogen and two oxygen atoms from three L_1 ligands. The coordination geometry can be described as a Jahn-Teller distorted pyramid with the τ value²⁴ of 0.252 for **1** or 0.215 for **2**. The apical position for each Cu(II) center is occupied by one nitrogen atom of imidazole ring, where the Cu–N bond length is significantly longer than those Cu–O (phenolic oxygen atoms) and Cu–N (Schiff-base nitrogen atoms) ones in the coordination plane. The dihedral angle between the imidazole and the phenolic rings within ligands L_1 or L_2 is $80.1(1)^\circ$ or $84.3(5)^\circ$. In contrast, the dihedral angle between the two coordinated phenolic rings within the basal coordination plane is $11.9(1)^\circ$ in **1** or $11.8(5)^\circ$ in **2**, and that between the two coordinated imidazole rings is $24.8(1)^\circ$ or $24.3(5)^\circ$. It is noted that four L_1 and L_2 ligands in **1** and **2** can be divided into two groups. Half of them serve as the bidentate ligands, while the other half act as the tridentate ones. The two copper(II) centers are separated by two flexible N-(3-aminopropyl)imidazole units with the separation between them of $9.202(3)\text{ Å}$ in **1** or $9.151(11)\text{ Å}$ in **2**.

X-ray structural analysis for complex **3** exhibits that it is also a dinuclear Cu(II) compound. However, each Cu(II) ion is four-coordinated by two phenolic oxygen atoms and piperidine nitrogen atom from one ligand as well as one imidazole nitrogen atom from the other ligand, showing square planar coordination geometry. The dihedral angles between the imidazole and two phenolic rings are $28.6(2)^\circ$ and $29.7(2)^\circ$, and the distance between two Cu(II) centers is $5.637(4)\text{ Å}$. It is interesting to point out that an unusual 2,6-diphenolic piperidine based multidentate ligand L_3 is *in situ* formed where the original Schiff-base C=N double bond disappears. Different from the half-bidentate and half-tridentate monovalent ligands L_1 and L_2 in **1** and **2**, the

divalent anionic ligand L_3 in **3**, which is suggested to come from the flexible Schiff-base ligand HL_1 with the participancy of methanol and acetone, displays a tetradentate coordination fashion.

In summary, two new flexible Schiff-base ligands HL_1 and HL_2 were prepared via the condensation between 3,5-dichlorosalicylaldehyde/3,5-dibromosalicylaldehyde and *N*-(3-aminopropyl)imidazole. The reactions between HL_1/HL_2 and $Cu(OAc)_2 \cdot 2H_2O/NH_3 \cdot H_2O$ in the mixture of methanol and acetone solvents yield two dinuclear five-coordinate $Cu(II)$ complexes formulated as $[Cu_2(L_1)_4]$ (**1**) and $[Cu_2(L_2)_4]$ (**2**), respectively, in which two of the L_1 and L_2 ligands are tridentate and the other two are bidentate. It is very interesting to mention that an unprecedented dinuclear four-coordinate $Cu(II)$ complex formulated as $[Cu_2(L_3)_2] \cdot 2H_2O$ (**3**) is obtained as a by-product of this reaction, where the tetradentate ligand H_2L_3 having an *in situ* formed 2,6-diphenolic piperidine ring.

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Notes and references

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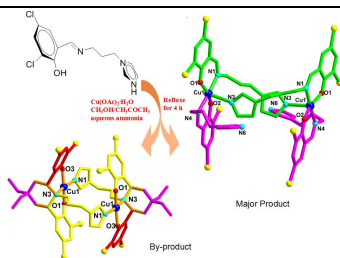
† Electronic Supplementary Information (ESI) available: Syntheses of Schiff-base ligands HL_1 and HL_2 , FT-IR, ESI-MS, ¹H and ¹³C NMR, UV-Vis and PXRD spectra, together with Table of selected bond angles and hydrogen bonds for related compounds. CCDC: 995477-995479. For crystallographic data in CIF or other electronic format See DOI:10.1039/b000000x/

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- Syntheses of dinuclear copper(II) complexes **1-3**. Complex **1**: HL_1 (0.062 g, 0.20 mmol) was dissolved in the acetone/methanol mixture ($v/v = 2:1$, 15 cm^3), and excess $NH_3 \cdot H_2O$ was added. The mixture was added a solution of $Cu(OAc)_2 \cdot H_2O$ (0.020 g, 0.10 mmol) in acetone (10 cm^3) and refluxed for 4 h. After that, the solution was cooled to room temperature and filtered. The filtrate was allowed to evaporate slowly for two weeks in air at room temperature, and green microcrystals of **1** were obtained in a yield of 0.088 g (67 % based on $Cu(II)$ ion). Main FT-IR absorptions (KBr, cm^{-1}): 3443 (w), 2858 (w), 1411 (s), 1218 (vs), 1030 (m), 705 (m). *Anal. Calc.* for $C_{52}H_{48}Cl_8Cu_2N_{12}O_4 \cdot 2H_2O$: C, 46.20; H, 3.88; N, 12.43 %. Found: C, 46.61; H, 3.85; N, 12.58 %. UV-Vis in methanol, $\lambda_{max} = 423$ and 332 nm. Single crystals of **3** suitable for X-ray diffraction determination was obtained as a dark-green by-product in a yield of 0.030 g (23 % based on $Cu(II)$ ion), together with the main product **1** in the same beaker. Main FT-IR absorptions (KBr, cm^{-1}): 3433 (w), 2912 (w), 2854 (w), 1710 (w), 1512 (m), 1454 (vs), 1147 (s), 705 (m). *Anal. Calc.* for $C_{50}H_{54}Cl_8Cu_2N_6O_{10}$: C, 45.85; H, 4.16; N, 6.42 %. Found: C, 45.57; H, 3.99; N, 6.18 %. UV-Vis in DMF, $\lambda_{max} = 428$ and 334 nm. Complex **2**: The synthesis of **2** was similar to that of **1**. Yield: 0.116 g (68 % based on $Cu(II)$ ion). Main FT-IR absorptions (KBr, cm^{-1}): 3442 (w), 2857 (w), 1411 (vs), 1286 (vs), 1029 (s), 751 (m). *Anal. Calc.* for $C_{52}H_{48}Br_8Cu_2N_{12}O_4 \cdot 2H_2O$: C, 36.58; H, 3.07; N, 9.84 %. Found: C, 36.79; H, 2.70; N, 10.09 %. UV-Vis in methanol, $\lambda_{max} = 425$ and 336 nm.
- Crystallographic data: **1**, formula, $C_{52}H_{48}Cl_8Cu_2N_{12}O_4$, $M_r = 1315.72$, monoclinic space group, $P2_1/c$, $a = 12.946(2)$, $b = 13.680(2)$, $c = 19.492(4)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 114.307(2)^\circ$, $V = 3146.0(9)$ Å³, $Z = 2$, $D_c = 1.389$ g·cm⁻³, crystal size (mm) = 0.08 x 0.10 x 0.12, $S = 1.07$, $R_1 = 0.0550$ and $wR_2 = 0.1647$. **2**, formula, $C_{52}H_{48}Br_8Cu_2N_{12}O_6$, $M_r = 1703.32$, monoclinic space group $P2_1/c$, $a = 12.949(10)$, $b = 14.283(12)$, $c = 19.337(12)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 114.18(4)^\circ$, $V = 3263(4)$ Å³, $Z = 2$, $D_c = 1.701$ g·cm⁻³, crystal size (mm) = 0.10 x 0.10 x 0.12, $S = 1.06$, $R_1 = 0.0939$ and $wR_2 = 0.2451$. **3**, formula, $C_{50}H_{54}Cl_8Cu_2N_6O_{10}$, $M_r = 1309.69$, monoclinic space group $P2_1/n$, $a = 8.722(7)$, $b = 18.004(13)$, $c = 18.378(14)$ Å, $\alpha = \gamma = 90.00^\circ$, $\beta = 99.404(10)^\circ$, $V = 2847(4)$ Å³, $Z = 2$, $D_c = 1.528$ g·cm⁻³, crystal size (mm) = 0.10 x 0.12 x 0.16, $S = 0.87$, $R_1 = 0.0628$ and $wR_2 = 0.1700$.
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Table of Content

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A dinuclear Cu(II) complex **3**, having a unprecedented *in situ* formed 2,6-piperidin-4-one based multidentate ligand produced from the flexible Schiff-base ligand HL₁, can be yielded as a side product in the presence of Cu(OAc)₂·H₂O/NH₃·H₂O dissolved in methanol/acetone, in addition to the expected dinuclear Cu(II) complex **1**.