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

Yuan Dai,^a Yin-Ge Wang,^b Jiao Geng,^a Yu-Xin Peng^a and Wei Huang^{*a}

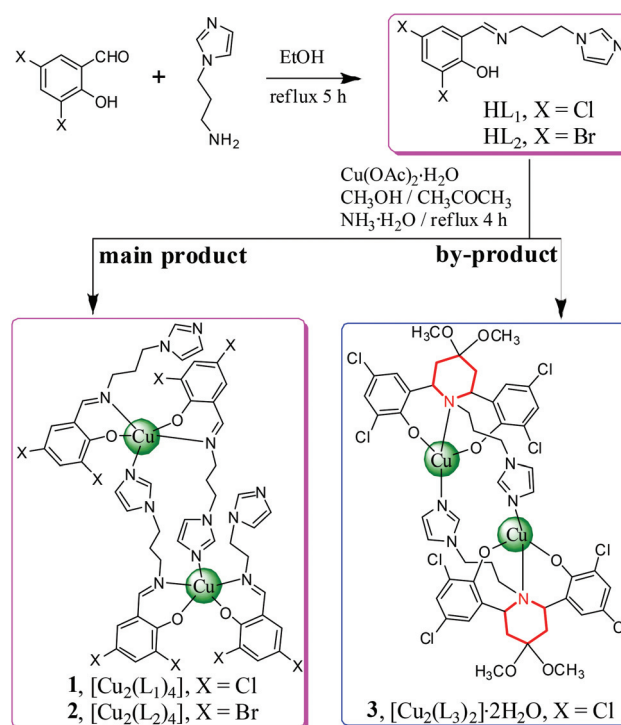
A dinuclear Cu(II) complex $[\text{Cu}_2(\text{L}_3)_2]\cdot 2\text{H}_2\text{O}$, having an unprecedented *in situ* formed diphenolate 2,6-piperidin-4-one derived ligand produced from the flexible Schiff-base ligand HL_1 , can be yielded as a side product in the presence of $\text{Cu}(\text{OAc})_2\cdot\text{H}_2\text{O}-\text{NH}_3\cdot\text{H}_2\text{O}$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

Schiff bases are important ligands and 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 most extensively studied topics in modern coordination chemistry. Recent researches show that Schiff-base complexes have various applications such as anti-cancer 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 previously investigated.^{16–18} The construction of Schiff-base complexes can be regarded as metal-assisted self-assembly, which is commonly reported in literature.¹⁹

In our previous work, a series of Schiff-base macrocyclic metal complexes bearing salicylaldehyde-based components were reported.²⁰ In addition, a Schiff-base ligand obtained from the condensation between salicylaldehyde and *N*-(3-aminopropyl)imidazole, exhibiting multifarious coordination types with copper(II) and cadmium(II), has been investigated.²¹ As further investigation of this work, we report here 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 arise 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



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

^aState Key Laboratory of Coordination Chemistry, Nanjing National Laboratory of Microstructures, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, P. R. China. E-mail: whuang@nju.edu.cn

^bCollege of Sciences, Nanjing Tech University, Nanjing, 210009, P. R. China

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reaction between *N*-(3-aminopropyl)imidazole and 3,5-dichloro-salicylaldehyde/3,5-dibromosalicylaldehyde, where several drops of glacial acetic acid were 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 a 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 as the reaction proceeds, and it reaches a maximum of 23% after 4 h refluxing with the formation of crystal 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 the ring formation reaction of L_2 is considerably lower because 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.

In the FT-IR spectra of HL_1 and HL_2 (Fig. S11 and S12[†]), a strong absorption peak is observed for each at 1632 and 1641 cm^{-1} , indicating the formation of the Schiff-base $\text{C}=\text{N}$ unit. In contrast, such a band is shifted to 1623 cm^{-1} in complexes **1** and **2** (Fig. S13 and S14[†]), reflecting the influence of metal-ion complexation on the coordinated $\text{C}=\text{N}$ unit. However, such a strong peak cannot be observed in the FT-IR spectrum of complex **3** (Fig. S15[†]), suggesting the disappearance of the $\text{C}=\text{N}$ moiety of the *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. S16 and S17[†]). However, it is difficult for us to obtain high quality ESI-MS spectra of all the three dinuclear $\text{Cu}(\text{II})$ complexes.

UV-vis absorption spectra of complexes **1–3** have been compared with those of the corresponding ligands HL_1 and HL_2 , as can be seen in Fig. S12,[†] 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 . The former for each is assigned to the $\pi-\pi^*$ electronic transition of the phenolic ring, while the latter is attributed to the $\pi-\pi^*$ 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–d transition absorption peak emerges at 423 and 425 nm for each complex. In comparison with **1** and **2**, the broad d–d transition absorption peak of **3** is slightly red-shifted to 428 nm. Furthermore, the phase purity of dinuclear $\text{Cu}(\text{II})$ complexes **1–3** has been confirmed by the PXRD patterns (Fig. S13–S15[†]), in which the simulated and as-synthesized spectra are almost the same.

ORTEP diagrams with the numbering schemes of the molecular structures of three dinuclear $\text{Cu}(\text{II})$ complexes are given in Fig. 1.²³ X-ray single-crystal diffraction studies for **1** and **2**

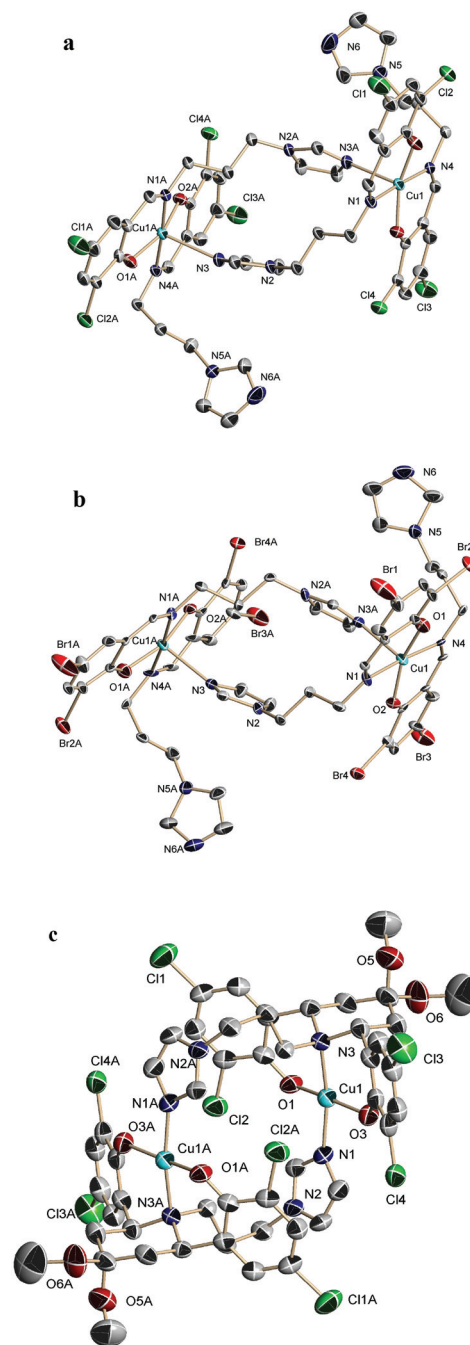


Fig. 1 ORTEP diagrams (30% thermal probability level ellipsoids) of the molecular structures of three dinuclear $\text{Cu}(\text{II})$ complexes **1** (a), **2** (b) and **3** (c) with the atom-numbering scheme. Selected bond lengths (Å): **1**: Cu1–O1, 1.920(3), Cu1–O2, 1.919(2), Cu1–N1, 2.035(3), Cu1–N4, 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*.

reveal that each $\text{Cu}(\text{II})$ 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 posi-

tion for each Cu(II) center is occupied by one nitrogen atom of the imidazole ring, where the Cu–N bond length is significantly longer than those of Cu–O (phenolic oxygen atoms) and Cu–N (Schiff-base nitrogen atoms) 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 $24.8(1)$ or $24.3(5)^\circ$. Note that four L_1 and L_2 ligands in **1** and **2** can be divided into two groups. Half of them serve as bidentate ligands, while the other half act as tridentate ligands. The two copper(II) centers are separated by two flexible N-(3-amino-propyl)imidazole units with the separation between them of $9.202(3)$ Å in **1** or $9.151(11)$ 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 the Cu(II) centers is $5.637(4)$ 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 arise from the flexible Schiff-base ligand HL_1 with the participating 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-amino-propyl)imidazole. The reactions between HL_1/HL_2 and $Cu(OAc)_2 \cdot 2H_2O \cdot NH_3 \cdot H_2O$ 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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- 22 Syntheses of dinuclear copper(II) complexes **1**–**3**. Complex **1**: HL_a (0.062 g, 0.20 mmol) was dissolved in the acetone–methanol mixture (v/v = 2 : 1, 15 cm³) and excess NH₃·H₂O was added. The mixture was added to a solution of Cu(OAc)₂·H₂O (0.020 g, 0.10 mmol) in acetone (10 cm³) 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 C₅₂H₄₈Cl₈Cu₂N₁₂O₄·2H₂O: C, 46.20; H, 3.88; N, 12.43%. Found: C, 46.61; H, 3.85; N, 12.58%. UV-Vis in methanol, λ_{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 C₅₀H₅₄Cl₈Cu₂N₆O₁₀: C, 45.85; H, 4.16; N, 6.42%. Found: C, 45.57; H, 3.99; N, 6.18%. UV-Vis in DMF, λ_{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 C₅₂H₄₈Br₈Cu₂N₁₂O₄·2H₂O: C, 36.58; H, 3.07; N, 9.84%. Found: C, 36.79; H, 2.70; N, 10.09%. UV-Vis in methanol, λ_{max} = 425 and 336 nm.
- 23 Crystallographic data: **1**, formula, C₅₂H₄₈Cl₈Cu₂N₁₂O₄, M_r = 1315.72, monoclinic space group, *P*2/*c*, *a* = 12.946(2), *b* = 13.680(2), *c* = 19.492(4) Å, α = γ = 90°, β = 114.307(2)°, *V* = 3146.0(9) Å³, *Z* = 2, *D*_c = 1.389 g cm⁻³, crystal size (mm) = 0.08 × 0.10 × 0.12, *S* = 1.07, *R*₁ = 0.0550 and *wR*₂ = 0.1647. **2**, formula, C₅₂H₄₈Br₈Cu₂N₁₂O₆, M_r = 1703.32, monoclinic space group *P*2/*c*, *a* = 12.949(10), *b* = 14.283(12), *c* = 19.337(12) Å, α = γ = 90°, β = 114.18(4)°, *V* = 3263(4) Å³, *Z* = 2, *D*_c = 1.701 g cm⁻³, crystal size (mm) = 0.10 × 0.10 × 0.12, *S* = 1.06, *R*₁ = 0.0939 and *wR*₂ = 0.2451. **3**, formula, C₅₀H₅₄Cl₈Cu₂N₆O₁₀, M_r = 1309.69, monoclinic space group *P*2₁/*n*, *a* = 8.722(7), *b* = 18.004(13), *c* = 18.378(14) Å, α = γ = 90.00, β = 99.404(10)°, *V* = 2847(4) Å³, *Z* = 2, *D*_c = 1.528 g cm⁻³, crystal size (mm) = 0.10 × 0.12 × 0.16, *S* = 0.87, *R*₁ = 0.0628 and *wR*₂ = 0.1700.
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