Dinuclear Cu(II) complexes based on two 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 [Cu2(L3)2]·2H2O, having an unprecedented in situ formed diphenolate 2,6-piperidin-4-one derived ligand produced from the flexible Schiff-base ligand HL2, can be yielded as a side product in the presence of Cu(OAc)2·H2O–NH3·H2O dissolved in methanol and acetone in addition to the expected dinuclear Cu(II) complex [Cu2(L1)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 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 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, HL1 and HL2, derived from the condensation between dihalogen substituted salicylaldehyde and N-(3-aminopropyl)-imidazole, and their dinuclear five-coordinate Cu(II) complexes formulated as [Cu2(L1)4] (1) and [Cu2(L2)4] (2), respectively, in which two of the L1 and L2 ligands are tridentate and the other two are bidentate. Furthermore, a unique tetratdentate divalent anionic ligand L3 including an in situ formed piperidine ring is obtained, which is suggested to arise from the monovalent anionic ligand L1. As a result, another dinuclear Cu(II) complex 3 with the formula of [Cu2(L3)2]·2H2O has been produced, where the Schiff-base C=N unit in ligand L1 disappears.

As shown in Scheme 1, two flexible Schiff-base ligands HL1 and HL2 were prepared in high yields by the condensation

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

†Electronic supplementary information (ESI) available: Syntheses of Schiff-base ligands HL1 and HL2, 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 ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt01014k
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 \(\text{Cu(OAc)}_2\cdot\text{H}_2\text{O}\) 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. SI1 and SI2†), 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 contrast, such a band is shifted to 1623 cm\(^{-1}\) in complexes 1 and 2 (Fig. SI3 and SI4†), reflecting the influence of metal-ion complexation on the coordinated C=N unit. However, such a strong peak cannot be observed in the FT-IR spectrum of complex 3 (Fig. SI5†), suggesting the disappearance of the C=N moiety of the \textit{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 SI7†). However, it is difficult for us to obtain high quality ESI-MS spectra of all the three dinuclear Cu(u) 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. 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 \(HL_2\). 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(u) 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 Cu(u) complexes 1–3 has been confirmed by the PXRD patterns (Fig. SI13–SI15†), 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 Cu(u) 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, 2.38(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.

Fig. 1 ORTEP diagrams (30% thermal probability level ellipsoids) of the molecular structures of three dinuclear Cu(u) 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 Cu(u) 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 \(\tau\) value\(^{24}\) 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 signifi-
cantly 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 L1 or L2 is 80.1(1)^° or 84.3(5)^°. In contrast, the dihedral angle between the two coordinative phenolic rings within the basal coordination plane is 11.9(1)^° in 1 or 11.8(5)^° in 2, and that between the two coordinative imidazole rings is 24.8(1) or 24.3(5)^°. Note that four L1 and L2 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 coordi-
nation geometry. The dihedral angles between the imidazole and two phenolic rings are 28.6(2)^° and 29.7(2)^°, and the dis-
tance between two the Cu(II) centers is 5.637(4) Å. It is interest-
ing to point out that an unusual 2,6-diphenolic piperidine
based multidentate ligand L3 is in situ formed where the orig-
inal Schiff-base C=N double bond disappears. Different from the half-bidentate and half-tridentate monovalent ligands L1
and L2 in 1 and 2, the divalent anionic ligand L3 in 3, which is suggested to arise from the flexible Schiff-base ligand HL1, with the participating of methanol and acetone, displays a tetraden-
tate coordination fashion.

In summary, two new flexible Schiff-base ligands HL1 and HL2 were prepared via the condensation between 3,5-dichlorosalicylaldehyde/3,5-dibromosalicylaldehyde and N-(3-amino-
propyl)imidazole. The reactions between HL1/HL2 and Cu-
(OAc)$_2$·2H$_2$O-NH$_2$H$_2$O in the mixture of methanol and acetone solvents yield two dinuclear five-coordinate Cu(II) com-
plexes formulated as [Cu$_2$(L$_1$)$_2$](1) and [Cu$_2$(L$_2$)$_2$](2), respect-
ively, in which two of the L1 and L2 ligands are tridentate and the other two are bidentate. It is very interesting to mention
that an unprecedented dinuclear four-coordinate Cu(II) com-
plex formulated as [Cu$_2$(L$_3$)$_2$]·2H$_2$O (3) is obtained as a by-
product of this reaction, where the tetradentate ligand H$_2$L$_3$
has an in situ formed 2,6-diphenolic piperidine ring.

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Notes and references


22 Syntheses of dinuclear copper(II) complexes 1–3. Complex 1: HL₃ [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 (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 (s), 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, C₅₂H₄₈Cl₈Cu₂N₁₂O₄·2H₂O, M_r = 1315.72, monoclinic space group, P2₁/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, R₁ = 0.0550 and wR₂ = 0.1647. 2, formula, C₅₂H₄₈Br₈Cu₂N₁₂O₄·2H₂O, M_r = 1703.32, monoclinic space group P2₁/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, R₁ = 0.0939 and wR₂ = 0.2451. 3, formula, C₅₀H₅₄Cl₈Cu₂N₆O₁₀·2H₂O, M_r = 1309.69, monoclinic space group P2₁/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, R₁ = 0.0628 and wR₂ = 0.1700.