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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 [Cu₂(L₁)₂](L₂)·2H₂O, having an unprecedented in situ formed diphenolate 2,6-piperidin-4-one derived 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 and acetone, besides the expected dinuclear Cu(II) complex [Cu₂(L₂)₂].

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-amino npropyl)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 HL₁ and HL₂, derived from the condensation between dihalogen substituted salicylaldehyde and N-(3-amino npropyl)imidazole, and their dinuclear five-coordinate Cu(II) complexes formulated as [Cu₂(L₁)₂] (1) and [Cu₂(L₂)₂] (2), respectively, in which two of the L₁ and L₂ ligands are tridentate and the other two are bidentate. Furthermore, a unique tetradeinate divalent anionic ligand L₃ including an in situ formed piperidine ring is obtained, which is suggested to come 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 reaction between N-(3-amino npropyl)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 Cu(OAc)₂·H₂O 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 L₂ 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 HL₁ and HL₂ (Fig. SI1 and Fig. 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
contract, such a band is shifted to 1623 cm\(^{-1}\) in complexes 1 and 2 (Fig. S13 and Fig. S14), 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. S15), suggesting the disappearance of C=N moiety of in situ formed ligand \(L_1\) after metal-ion complexation. In addition, negative ESI-MS spectra of \(L_1\) and \(L_2\) clearly show the presence of a molecular ion peak with 100% ion abundance (Fig. S16 and Fig. S17). 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. 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 \(HL_2\), respectively. The former for each is assigned as the \(\pi-\pi^*\) electronic transition of the phenolic ring, while the latter is attributed to the presence of a molecular ion peak with 100% ion abundance (Fig. S16 and Fig. S17). However, it is difficult for us to obtain high quality spectra of all three dinuclear Cu(II) complexes.

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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.
divalent anionic ligand L₁ in 3, which is suggested to come from the flexible Schiff-base ligand HL₃ with the participancy of methanol and acetone, displays a tetradsentate 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-aminopropyl)imidazole. The reactions between HL₁/HL₂ and Cu(OAc)₂·2H₂O/NH₃/H₂O in the mixture of methanol and acetone solvents yield two dinuclear five-coordinate Cu(II) complexes formulated as [Cu(L₁)L₂](₁) and [Cu(L₂)L₃](₂), respectively, 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) complex 3 formulated as [Cu(L₂)L₃]·2H₂O (3) is obtained as a by-product of this reaction, where the tetradsentate ligand HL₃ having an in situ formed 2,6-diphenolic pipe ring.

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Notes and references

3. 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 as 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 I 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 Cu₂H₂Cl₂Cu₂(OAc)₂·H₂O: C, 46.58; H, 3.82; N, 12.54 %. Found: C, 46.61; H, 3.85; N, 12.58 %. UV–Vis in methanol, λmax = 425 and 332 nm. Single crystals of 3 suitable for X-ray diffraction determination were obtained as a dark-green by-product in a yield of 0.030 g (25 % 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 Cu₂H₂Cl₂Cu₂(OAc)₂·H₂O: C, 45.85; H, 4.16; N, 6.42 %. Found: C, 45.57; H, 3.99; N, 6.18 %. UV–Vis in DMF, λmax = 428 and 334 nm. Complex 2: The synthesis of 2 was similar to that of I. Yield: 0.116 g (68 % based on Cu(II) ion). Main FT–IR absorptions (KBr, cm⁻¹): 3442 (w), 2857 (w), 1411 (vs), 1286 (m), 1029 (s), 751 (m). Anal. Calc. for Cu₂H₂Br₂Cu₂(OAc)₂·2H₂O: C, 36.58; H, 3.07; N, 9.84 %. Found: C, 36.79; H, 2.70; N, 10.09 %. UV–Vis in methanol, λmax = 425 and 336 nm.

Crystallographic data: I, formula, Cu₂H₂Cl₂Cu₂(OAc)₂·H₂O, Mr = 1315.72, monoclinic space group, P2₁/c, a = 12.946(2) Å, b = 13.680(2) Å, c = 19.492(4) Å, β = 90 °, V = 31460.0(9) Å³, Z = 2, Dc = 1.389 g cm⁻³, crystal size (mm) = 0.08 x 0.10 x 0.12, S = 1.07, R₁ = 0.0550 and wR₁ = 0.1647, 2, formula, Cu₂H₂Br₂Cu₂(OAc)₂·Mr = 1703.32, monoclinic space group P2₁/c, a = 12.949(10) Å, b = 14.283(12) Å, c = 19.337(12) Å, α = 90 °, β = 114.18(4) °, V = 3263(4) Å³, Z = 2, Dc = 1.701 g cm⁻³, crystal size (mm) = 0.10 x 0.10 x 0.12, S = 1.06, R₁ = 0.0939 and wR₁ = 0.2451. 3, formula, Cu₂H₂Cl₂Cu₂(OAc)₂·Mr = 1309.69, monoclinic space group P2₁/n, a = 8722(7) Å, b = 18.004(13), c = 18.378(14) Å, α = 90 °, β = 99.404(10) °, V = 2847(4) Å³, Z = 2, Dc = 1.528 g cm⁻³, crystal size (mm) = 0.10 x 0.12 x 0.16, S = 0.87, R₁ = 0.0628 and wR₁ = 0.1700.
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 HL, can be yielded as a side product in the presence of Cu(OAc)$_2$·H$_2$O/NH$_3$·H$_2$O dissolved in methanol/acetone, in addition to the expected dinuclear Cu(II) complex 1.

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