

## Synthesis and structure of neutral double helicate

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A new approach to generating supramolecular architectures, based on easy-to-prepare schiff base ligands, is described together with its application to the self-assembly of supramolecular neutral double helicates.

**Keywords** Self-assembly, Schiff base, helical complex

Ongoing interests are based on the supramolecular synthetic approach and its application to the quest to control molecular architecture. Self-assembly and molecular recognition appear to be essential features for the construction of supramolecular architectures utilizing the formation of non-covalent bonds in solution.<sup>1</sup> However, one drawback to this metallo-supramolecular procedure was that the almost exclusive of ligand systems were constructed from polypyridyl,<sup>2,3</sup> benzimidazole<sup>4</sup> and catechol<sup>5</sup> binding sites. Since the helical complexes have been greatly improved during the past years, bidentate ligands used to form helicate need multiple-step synthesis and some of which are expensive materials. Thus, this drawback limits their further potential usage. If supramolecular chemistry is to achieve its full potential, it is desirable that inexpensive and easy-to-prepare systems be developed. In addition, the helical complexes reported up to date mostly bear positive or negative charges. While neutral helicates are very limited with few exceptions,<sup>6</sup> and this can be attributed to the inappropriate ligands.

In order to allow for helical complex, the ligand should contain at least two metal binding sites, which are separated by a spacing group which must be sufficiently structured to ensure that the different binding sites cannot coordinate the same metal ion.<sup>7</sup> Just recent-

ly, Hannon<sup>8</sup> and Yoshida<sup>9</sup> reported that  $L_1$  with Ni(II) and Zn(II) self-assembled into triple-helical complexes in appropriate conditions, respectively. Considering that the salen Schiff base is easy-preparation get and has *N*, *O*-bidentate to chelate many transition metal ions,<sup>10</sup> we have prepared the ligands  $L_2$  and  $L_3$  (see Fig. 1). The incorporated phenylene groups sterically prevent the two metal binding sites from coordinating to a single metal center. As ligands  $L_2$  and  $L_3$  coordinate to copper(II) ion, the hydroxyl group will release proton with the addition of base. Consequently, the neutral complexes will be generated. Herein, we report the facile synthesis of neutral-helical copper(II) complex using  $L_2$  and cupric chloride.

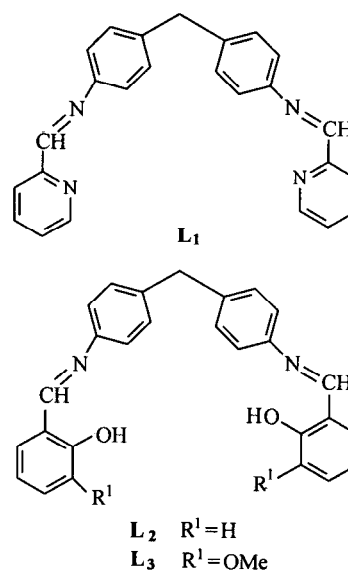


Fig. 1 Structures of related ligands.

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The ligands were prepared by simply mixing the metholic solutions of salicylaldehyde or *O*-vanillin and 4, 4'-methylenedianiline. On stirring at room temperature for 1 h and refluxing for another 2 h, the ligands precipitated from the reaction mixtures. The products can be isolated by filtration and washed with methanol for three times in high yields (85% and 70%, respectively). The ease of synthesis and high-yield reaction from commercial and inexpensive reagents make these extremely attractive helicates in self-assembly field.

Warming THF solutions containing 1 equiv. of ligand **L**<sub>1</sub> and 1 equiv. of CuCl<sub>2</sub> · 2H<sub>2</sub>O with 2 equiv. of triethyl amine at reflux for 1 h resulted in the formation of dark-brown solution. After cool and addition some drops of DMF and MeOH to the resulting mixture, the solution was kept by slow evaporation. After about one week, dark single crystal was obtained (yield about 35%). The structure of the neutral helicate was established by X-ray analysis and the results are shown in Fig. 2 and Table 1, which confirms the formation of the double helicate. The complex contains two copper(II) ions and two **L**<sub>2</sub> ligands. Each copper(II) center is

bound to two salicyladimine units to attain a pseudo-tetrahedral coordination geometry with Cu—O distance in the range of 0.1890(3)—0.1893(3) and Cu—N 0.1953(3)—0.1974(3) nm. Coordination to the metal center forces twisting between the phenylene ring and the salicyladimine unit, and the logical consequence is the formation of a double-helical array. The two copper(II) centers are separated by 1.19495(9) nm and the twisting of the phenylene units results in a aryl-lined cavity with the distance 0.4010 nm of plane 3 and 4 and 0.6219 nm of plane 3 and 6, generating a cavity with the potential to trap small molecules. Calculations indicate that there are no obvious face to face  $\pi$ -stacking interactions with the angle 23.62° between plane 3 and 4 and 18.55° between plane 6 and 5. The IR spectra show that the C = N absorption of free ligand 1618.8 cm<sup>-1</sup> decreases to 1612.2 cm<sup>-1</sup> in the metal complex, indicating the coordination of nitrogen to copper ion. DMF seems to play a role in the assembly of the double helicate and is very stable in the complex with the IR absorption of C = O 1666.8 cm<sup>-1</sup>.

**Table 1** Selected bond lengths (nm) and angle (°) for the helical complex

Cu(2)—O(4)	0.1894(3)	Cu(2)—O(3)	0.1894(3)
Cu(2)—N(4)	0.1952(3)	Cu(2)—N(2)	0.1964(3)
Cu(2)—Cu(1)	1.19495(9)	Cu(1)—O(2)	0.1890(3)
Cu(1)—O(1)	0.1894(3)	Cu(1)—N(3)	0.1969(3)
Cu(1)—N(1)	0.1974(3)		
O(4)-Cu(2)-O(3)	93.54(13)	O(4)-Cu(2)-N(4)	95.54(12)
O(3)-Cu(2)-N(4)	144.07(14)	O(4)-Cu(2)-N(2)	142.50(14)
O(3)-Cu(2)-N(2)	94.91(13)	N(4)-Cu(2)-N(2)	99.61(13)
O(4)-Cu(2)-Cu(1)	123.01(9)	O(3)-Cu(2)-Cu(1)	142.57(10)
O(2)-Cu(1)-O(1)	89.93(14)	O(2)-Cu(1)-N(3)	151.31(15)
O(1)-Cu(1)-N(3)	91.97(14)	O(2)-Cu(1)-N(1)	93.27(14)
O(2)-Cu(1)-N(1)	148.89(14)	N(3)-Cu(1)-N(1)	99.63(14)

We have synthesized the Ni(II), Mn(II), and Cd(II) complexes of **L**<sub>2</sub>. But they are insoluble in many organic solvents. To improve the solubility of such metal complexes, the methoxyl group was introduced into the Schiff base and **L**<sub>3</sub> was synthesized. Most of **L**<sub>3</sub>-metal complexes are soluble in common organic solvents, for example, the nickel complex is soluble in chloroform and copper complex is easily soluble in DMF or chloroform. Regretfully, we have not obtain good-quality crystals

for X-ray analysis.<sup>11</sup> It is known that the unsaturated copper-Schiff base complex can catalyze some kinds of organic reactions.<sup>12</sup> In addition, ligands like **L**<sub>3</sub> with nickel complexes can selectively self-assembly with alkali metal cations.<sup>13</sup> As such facts are considered, whether the substitutes in Schiff bases could effect the metal-ligand architectures or alkali metal cations could re-assembly the formed supramolecular complexes are interesting tasks to be further investigated.

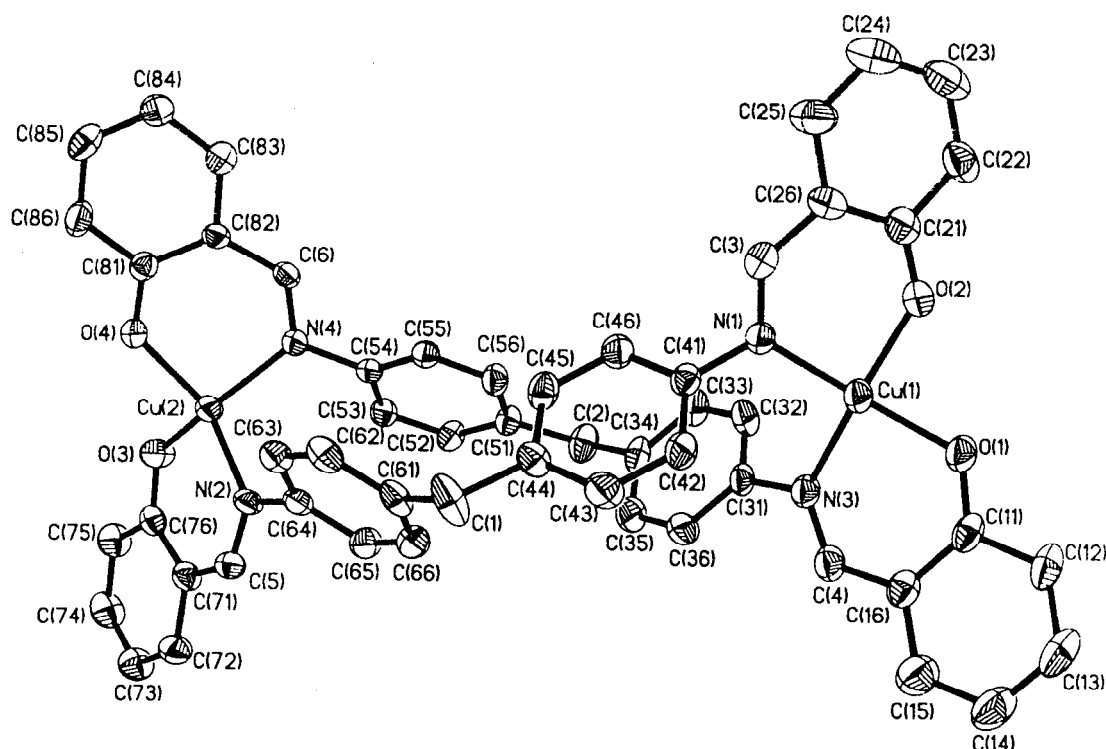


Fig. 2 Molecular structure of the neutral double-helical complex.

## References

$L_2$   $\delta_H$  (200 MHz,  $CDCl_3$ ): 4.01 (m, 2H), 6.91—7.39 (b, 16H), 8.60 (m, 2H).  $\nu_{max}$ : 3440, 3023, 1618, 1579,  $751\text{cm}^{-1}$ .  $m/z$ : 406.1(406.5). Anal.  $C_{27}H_{22}N_2O_2$ . Calcd: C, 79.72; N, 6.89; H, 5.45. Found: C, 79.78; N, 7.09; H, 5.67.

$L_3$   $\delta_H$  (200 MHz,  $CDCl_3$ ): 3.91 (s, 6H), 4.01 (m, 2H), 6.90—7.23 (b, 14), 8.62 (m, 2H).  $\nu_{max}$ : 1618, 1597, 1257,  $731\text{cm}^{-1}$ .  $m/z$ : 467.0(466.5). Anal.  $C_{29}H_{26}N_2O_4$ . Calcd: C, 74.66; N, 6.00; H, 5.62. Found: C, 74.45; N, 5.839; H, 6.02.

$Cu_2(L_2)_2 \cdot DMF$   $\nu_{max}$ : 3021, 1668, 1612, 1588,  $762\text{cm}^{-1}$ . Calcd: C, 67.84; N, 6.94; H, 4.66. Found: C, 67.44; N, 7.09; H, 5.26.

Crystal data for  $Cu_2(L_2)_2 \cdot DMF$ ;  $C_{57}H_{47}Cu_2N_5O_5$ ,  $M = 1009.08$ , orthorhombic, space group  $pbca$ ,  $a = 2.68454(17)$ ,  $b = 1.22592(8)$ ,  $c = 2.9290(2)$  nm,  $U = 9.6393(11)$  nm<sup>3</sup>,  $Z = 8$ ,  $T = 292(2)$  K,  $\mu = 0.938$  mm<sup>-1</sup>. Goodness-of-fit on  $F^2$  was 0.914.  $R1$  [for  $I > 2\sigma(I)$ ] = 0.0488,  $wR2 = 0.0986$ . The structure was solved by direct methods using SHELXTL-97.

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