

# Self-assembling tetranuclear copper(II) complex of a bis-bidentate Schiff base: double-helical structure induced by aromatic $\pi\cdots\pi$ and $\text{CH}\cdots\pi$ interactions

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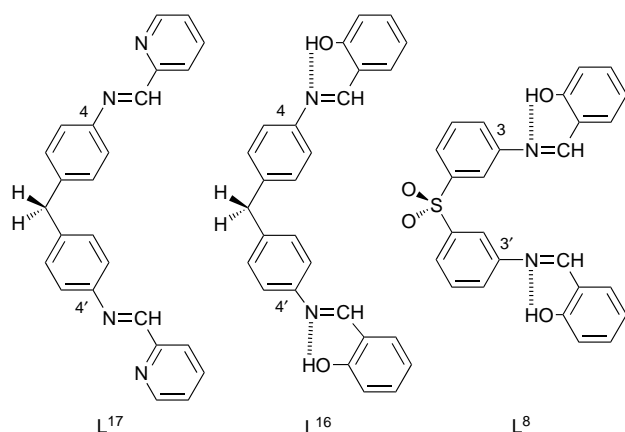
The synthesis and structure of a tetranuclear copper(II) complex of a bis-N,O-bidentate Schiff base is reported; two types of copper(II) centers and the preference for two conformational degrees of freedom in the ligand lead to the unique formation of a novel supramolecular architecture not requiring a preorganized synthetic approach.

Self-assembly and molecular recognition appear to be essential factors for the construction of supramolecular architectures utilizing the formation of non-covalent bonds in solution.<sup>1</sup> The use of metal ions with specific preferences for particular coordination geometries has been developed rapidly in order to produce non-covalently organized structures, resulting in self-assembly of target ligands.<sup>2</sup> Many types of oligopyridines have been used because of their preorganized characteristics in self-assembling processes.<sup>3</sup>

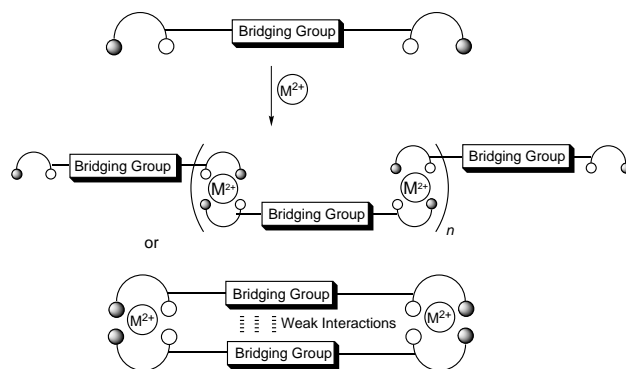
Recently, new ligand systems have been exploited to construct unprecedented structures formed by self-assembling processes in solution and in the solid phase.<sup>4,5</sup> The requirement of the supramolecular structure is principally controlled by the appropriate combination of various types of weak non-covalent interactions and the geometrical preference of the metal ion. Our recent investigation using bis-bidentate Schiff base ligands (Scheme 1) allows for the synthesis of a variety of metal-assisted supramolecular structures. A dinuclear triple-helical  $\text{Zn}^{\text{II}}$  complex of  $\text{L}^{\text{17}}$ ,<sup>5</sup> a dinuclear double-helical  $\text{Cu}^{\text{II}}$  complex of  $\text{L}^{\text{16}}$ ,<sup>6</sup> and polynuclear  $\text{Zn}^{\text{II}}$  complexes of  $\text{L}^{\text{16}}$ ,<sup>5</sup> have been synthesized.

Here we describe a novel and general strategy for the construction of metal-assisted supramolecular architectures using ligand  $\text{L}^{\text{8}}$ . This architecture is prepared readily utilizing the weak aromatic  $\pi\cdots\pi$  and  $\text{CH}\cdots\pi$  interactions operating between the bridging groups of the bis-bidentate Schiff bases (Scheme 2).

The Schiff base ligand  $\text{L}^{\text{8}}$  contains two N,O-bidentate chelating moieties linked *via* the azomethine groups with bis(3-



Scheme 1



Scheme 2

aminophenyl)sulfone (Scheme 1). Reaction of  $\text{L}^{\text{8}}$  with  $\text{Cu}(\text{MeCO}_2)_2 \cdot \text{H}_2\text{O}$  in a 1 : 1 molar ratio in hot ethanol (*ca.* 60–70 °C) afforded a light-green solid  $\mathbf{1}$ .<sup>†</sup> Elemental analysis suggests the formation of a  $\text{Cu}^{\text{II}} : \text{L}^{\text{8}}$  2 : 2 complex and fast-atom bombardment mass spectroscopy (FABMS) also indicated a 2 : 2 complex for  $\mathbf{1}$ .<sup>‡</sup> However, positive-ion electrospray MS (*m/z* 2073.5) suggested the existence of a 4 : 4 complex for  $\mathbf{1}$ . The electronic absorption spectrum of  $\mathbf{1}$  shows a  $\pi\text{-}\pi^*$  band at 379.5

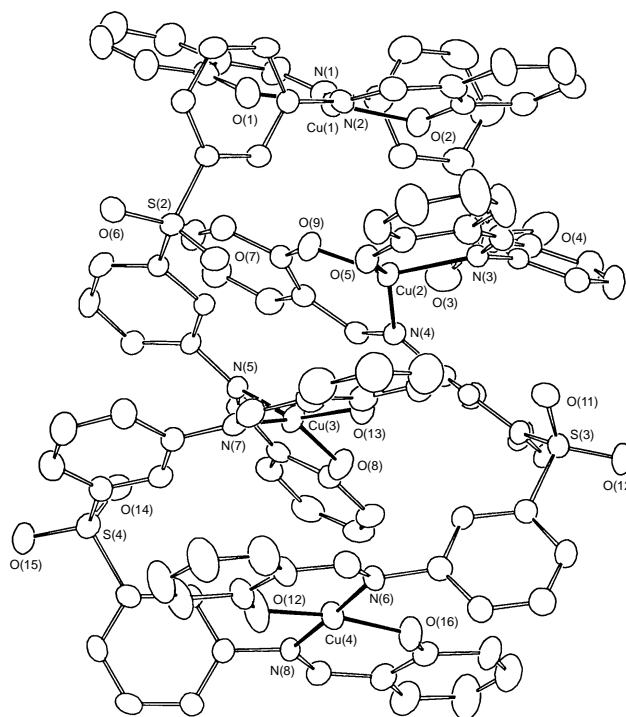


Fig. 1 Crystal structure of  $[\text{Cu}(\text{H-L}^{\text{8}})]_4 \mathbf{1}$

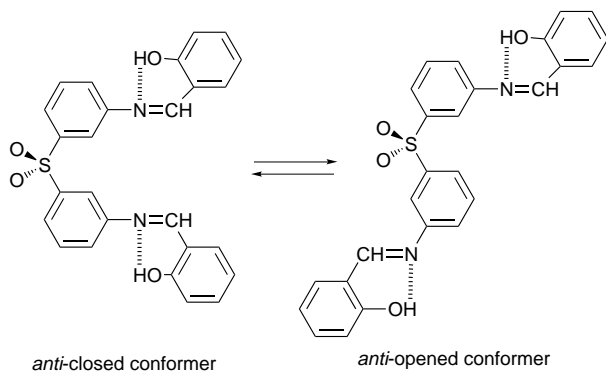


Fig. 2 Two main conformers of L<sup>8</sup>

nm in the visible region which indicates deprotonation of the OH groups and N,O-coordination of Cu<sup>II</sup>.<sup>7</sup>

Single crystals were obtained from chloroform–diethyl ether. An X-ray diffraction study confirms the formation of the Cu<sup>II</sup>:L<sup>8</sup> 4:4 structure as shown in Fig. 1.† The tetranuclear double helical structure appears to be stabilized by CH–π and π–π aromatic interactions (3.2–3.9 Å) between the bridging groups (–C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>–). Complex **1** contains four Cu<sup>II</sup> ions and four ligands. Two Cu<sup>II</sup> ions at the top [Cu(1)] and bottom [Cu(4)] of the tetranuclear (CuL<sup>8</sup>)<sub>4</sub> core adopt a square-planar (SP) coordination geometry, whereas the two remaining Cu<sup>II</sup> ions [Cu(2), Cu(3)] in the middle adopt a tetrahedral (T<sub>d</sub>) coordination geometry. Each Cu<sup>II</sup> ion is coordinated by N,O-bidentate sites originating from two different ligands. Each ligand interacts with two Cu<sup>II</sup> ions with a different coordination geometry. Furthermore, two types of conformations of L<sup>8</sup> are observed in this tetranuclear core (Fig. 2). The conformations of L<sup>8</sup>(1) and L<sup>8</sup>(4) are *anti*-closed ( $E_{\text{steric}} = -27.58 \text{ kcal mol}^{-1}$ , 1 cal = 4.184 J) (Fig. 2), whereas the conformations of L<sup>8</sup>(2) and L<sup>8</sup>(3) are similar and *anti*-opened ( $E_{\text{steric}} = -27.16 \text{ kcal mol}^{-1}$ ).¶

Fig. 3 shows selected bond lengths and angles around the four Cu<sup>II</sup> centers of the tetranuclear core of **1**. The Cu–N distances lie between 1.968(6)–2.024(6) Å and Cu–O is in the range 1.858(6)–1.903(5) Å. Angles O–Cu(1)–O, N–Cu(1)–N, N–Cu(1)–O [O–Cu(4)–O, N–Cu(4)–N, N–Cu(4)–O] are in the range 174.9(2), 171.4(2), 88.1(2)–91.4(2)° [170.4(3), 177.6(2), 88.6(2)–91.8°], respectively. Thus, the coordination geometries around Cu(1) and Cu(4) are almost square-planar. On the other hand, O–Cu(2)–O, N–Cu(2)–N, N–Cu(2)–O [O–Cu(3)–O, N–Cu(3)–N, N–Cu(3)–O] angles are 89.6(2), 99.2(2), 147.2(2)–148.8(2)° [89.2(2), 100.1(2), 144.6(2)–148.7(2)°] which show a distorted tetrahedral geometry around Cu(2) and Cu(3). Four Cu<sup>II</sup> ions having different coordination spheres lie almost in one plane and in a rhombus arrangement with Cu⋯Cu

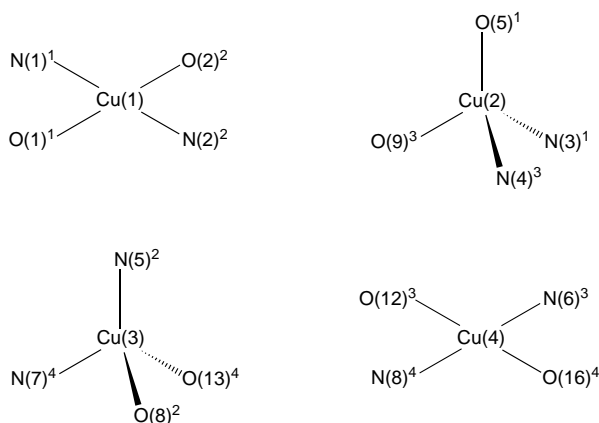


Fig. 3 Coordination geometries around the four Cu<sup>II</sup> ions of **1**

distances between 4.043 and 7.659 Å. The sum of the interior angles is 353.26°. Other metal complexes with Zn<sup>II</sup>, Ni<sup>II</sup> and Co<sup>II</sup> which are insoluble in most organic solvents appear to form (1:1)<sub>n</sub> polymeric structures (Scheme 2).

Flexible geometry of Cu<sup>II</sup> (SP or T<sub>d</sub>) and the flexible conformational freedom in the ligand lead to CH–π and π–π aromatic interactions between the bridging groups and the tetranuclear double-helical structure. These conformational preferences in the ligand and metal-coordination geometry are an unusual example in metallosupramolecular chemistry. The subtle change in the bridging group leads to an unprecedented organized structure in the absence of a preorganized synthetic approach. The development of new ligand systems using Schiff base series is now in progress.

## Footnotes and References

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† 3,3'-Diaminosulfone (0.5 mol) was added gradually to an EtOH solution (100 ml) of salicylaldehyde (1 mol) and the solution was stirred for 30 min at 60 °C and the orange solid precipitate was collected by filtration. Elemental analysis was in accord for L<sup>8</sup>. A mixture of L<sup>8</sup> (0.78 g, 1.72 mmol) and Cu<sup>II</sup>(MeCO<sub>2</sub>)<sub>2</sub>·H<sub>2</sub>O (0.34 g, 1.7 mmol) was dissolved in EtOH (100 ml) and heated and the resulting green powder was collected by filtration and washed with hot EtOH. This powder dissolves readily in DMF and CHCl<sub>3</sub>. X-Ray quality crystals were grown by slow diffusion of Et<sub>2</sub>O into a CHCl<sub>3</sub> solution of **1**. Satisfactory elemental analysis was obtained.

‡ MM2 force-field calculations also suggested the possibility for the existence of Cu<sup>II</sup>:L<sup>8</sup> 2:2 complexes, the minimum-energy self-assembling structures, **2** (SP–SP for two Cu<sup>II</sup>) and **3** (T<sub>d</sub>–T<sub>d</sub> coordination geometry). The force-field structure **3** ( $E_{\text{steric}} = -32.212 \text{ kcal mol}^{-1}$ ) is considerably more stable than that of **2** ( $E_{\text{steric}} = 8.662 \text{ kcal mol}^{-1}$ ); Tektronix CAChe System, (Version 3.7).

§ Crystal data for **1**: C<sub>104</sub>H<sub>72</sub>Cu<sub>4</sub>N<sub>8</sub>O<sub>16</sub>S<sub>4</sub>, 0.50 × 0.30 × 0.25 mm,  $M = 2072.18$ , brown prismatic crystal, monoclinic, space group P2<sub>1</sub>/c,  $a = 18.026(2)$ ,  $b = 23.450(3)$ ,  $c = 22.743(2)$  Å,  $\beta = 90.299(9)^\circ$ ,  $U = 9613(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.432 \text{ g cm}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 9.64 \text{ cm}^{-1}$ ,  $F(000) = 4240$ . 17 487 data collected at –100 °C on a Rigaku AFC 7S four circle diffractometer equipped with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structure was solved by direct methods with SHELX-86 (G. M. Sheldrick, University of Göttingen, 1986) and Fourier techniques, and refined by full-matrix least-squares on  $F^2$  data using SHELXL-93 (G. M. Sheldrick, University of Göttingen, 1993). and converged at  $R_1 = 0.0667$ ,  $wR_2 = 0.1652$ . CCDC 182/663.

¶ Although L<sup>8</sup> can adopt many conformations, molecular mechanics (MM2) calculations revealed the four minimum-energy structures as *anti*-closed and *anti*-opened conformers. These two isomers have almost the same energy. Other minimum-energy structures, *syn*-opened ( $E_{\text{steric}} = -27.4973 \text{ kcal mol}^{-1}$ ) and *syn*-closed ( $E_{\text{steric}} = -28.820 \text{ kcal mol}^{-1}$ ) conformers have similar energy.

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