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# Effect of Ligand Spacer on Metallosupramolecular Architectures: From a Dinuclear Copper(II) Double Helicate to a Tetranuclear Copper(II) Complex

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**Keywords:** Copper / Helical structures / Hydrogen bonds / N,O ligands / Solid-state structures

Two new bis(N,O-bidentate) Schiff base ligands with asymmetric spacers between the donor sites have been synthesized. The asymmetric ligand $H_2L^1$ self-assembles with copper(II) ions to give rise to a dinuclear copper(II) complex $[Cu_2L^1_2]$ (**1**), while a more flexible ligand $H_2L^2$, having an additional methylene group in the spacer, forms a tetranuclear copper(II) cluster $[Cu_4L^2_4]$ (**2**). Both complexes have been characterized by different analytical and spectroscopic techniques. Single-crystal X-ray diffraction study of **1** shows a dinuclear copper(II) double-stranded helicate with the two heterotopic ligands oriented head-to-head (HH), with a separation of 7.687(3) Å between the distorted tetrahedral copper(II) centers. The bis(bidentate) ligand strands wrap around the copper centers with a similar relative orientation (HH) to give rise to a double-helical structure. The intramolecular face-to-face π–π interaction stabilizes the double-helical structure of the molecule. In the tetranuclear complex **2**, the four copper(II) centers, separated by 7.288(2)–8.239(2) Å, define a slightly distorted tetrahedron.

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## Introduction

The synthesis of supramolecular clusters by spontaneous self-assembly of organic ligands and transition-metal ions has attracted much interest over the last few decades because of their potential application in magnetic, electrochemical, optical, and catalytic studies.[1] In the self-assembly process the constituent ligands and metals play important roles in the formation of metallosupramolecular clusters. Several structural motifs, prepared by transition-metal-directed self-assembly reactions, have been reported in the literature.[2] Among these, helical metallosupramolecular motifs have attracted much attention because of their presence in nature.[3–6] The basic feature to design helical supramolecular architectures is well established.[4,7,8] Other metallosupramolecular systems[1,9–11] reported in the literature include triangles,[12–16] squares,[17] tetrahedral,[18–24] capsules,[16,25–29] and other higher polyhedral geometries.[19,30–36] Tetrahedral clusters, the simplest polyhedron, are of special interest because of their structural speciality and host-guest chemistry. These clusters, in turn, give some insight in the design of high–symmetry, extended clusters. In addition, several factors are involved in predicting the self-assembly products. Apart from the geometric preference of the metal ion, the influence of the nature of the coordination sites, geometry of the ligand and other weak noncovalent interactions are equally important.

Most of the metallohelicates reported thus far employ polypyridine ligands.[5] Derivatives of beta-diketonates,[37] dipyrromethenes,[38–40] iminopyrroles,[41] and pyridyl Schiff bases[24,42–46] have been used as organic ligands for the synthesis of dinuclear clusters and clusters of higher nuclearity.[47,48] In contrast, very few Schiff-base-type iminophenol ligands have been reported for this purpose.[49–59] But there is no report on any supramolecular assembly formed by iminophenol Schiff base ligands with an asymmetric spacer between the bis(N,O-bidentate) metal binding sites.

The use of a suitable asymmetric spacer can prevent the two binding sites from coordinating the same metal ion, and in a dinuclear complex the ligands can assume two orientations, parallel or antiparallel. An antiparallel orientation of the ligand strands was observed in the double-stranded silver(I) complex in which a Schiff base ligand is derived from 4-aminobenzylamine and pyridine-2-aldehyde. This arrangement was explained on the basis of the geometrical requirements of the metal and ligand.[45] On the other hand, it has been proposed that the symmetric bis(iminophenol) ligands stabilize double-helical structures as a result of intra- and intermolecular noncovalent π–π, CH–π interactions.[54]

We report herein a strategy for the synthesis of metallosupramolecular assemblies of the copper(II) ion by using two new asymmetric bis(bidentate) ligands, $H_2L^1$ and $H_2L^2$. The asymmetric dianionic form of $H_2L^1$ can bind two metal

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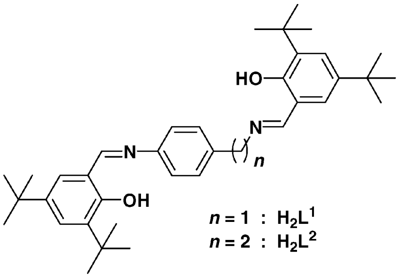
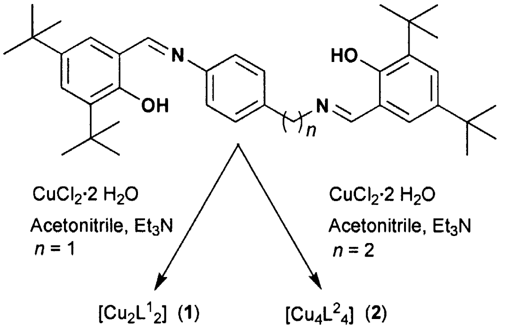
ions to form a dinuclear complex in a parallel (head-to-head) or antiparallel (head-to-tail) orientation. On the other hand, the $H_2L^2$ ligand, obtained by introducing another methylene group into the asymmetric spacer, should be more flexible. The synthesis, characterization, and crystal structures of a neutral double-helical copper(II) complex with the formula $[Cu_2L^1{}_2]$ (**1**) and of a neutral, tetrahedral tetranuclear copper(II) cluster with the formula $[Cu_4L^2{}_4]$ (**2**) are described in this work.



## Results and Discussion

The bis(bidentate) ligands $H_2L^1$ and $H_2L^2$ were synthesized in good yields by simple Schiff base condensation of one equivalent of the respective amines and two equivalents of 2,4-di-*tert*-butylsalicylaldehyde in ethanol at room temperature. The ligands were characterized by different analytical and spectroscopic techniques, along with the single-crystal X-ray structure of $H_2L^2$. Reactions of the ligands and $CuCl_2{\cdot}2H_2O$ in 1:1 ratio in acetonitrile afforded copper(II) complexes **1** and **2** (Scheme 1). In both the reactions, triethylamine was used as a base to deprotonate the phenol OH groups. The crude complexes thus obtained were recrystallized from a solvent mixture of dichloromethane and acetonitrile (1:1).



Scheme 1.

Elemental analysis data for **1** and **2** were found to be consistent with the 1:1 metal/ligand composition of the complexes. In the IR spectra of **1** and **2** (see Experimental Section), there are several strong bands in the region 3000–2850 cm$^{-1}$ assigned to the $\nu$(C–H) stretching modes of the *tert*-butyl groups on the phenol rings as observed also in the free ligand. The ligands show sharp peaks at around 1622 cm$^{-1}$, characteristic of the C=N stretching, that shifts to about 1616 cm$^{-1}$ upon complexation. This indicates the coordination of the imine nitrogen atoms to the copper centers. Electrospray Ionization (ESI) mass spectrometry was found to be a very important analytical tool for the characterization of the complexes, particularly with regard to the nuclearity and composition of **1** and **2**. ESI-MS of **1** in positive ion mode (in acetonitrile) shows peaks at $m/z$ = 1231.06 (30%) and 615.18 (100%) for **1**, with the expected isotope distribution patterns for $[Cu_2L^1{}_2]^+$ and $[CuL^1]^+$, respectively. This indicates the formation of a dinuclear copper(II) complex with $H_2L^1$. The ESI-MS of **2** shows peaks at $m/z$ = 1887.69 (10%), 1261.11 (20%), 630.23(80%), and 569.33 (100%), with the expected isotope distribution patterns for $[Cu_3L^2{}_3]^+$, $[Cu_2(HL^2)_2]^+$, $[Cu(HL^2)]^+$, and $[H_2L^2{+}H]^+$, which indicates the formation of a polynuclear copper(II) complex with nuclearity higher than two. The electronic spectra for **1** and **2** recorded in $CH_2Cl_2$ show strong phenolate-to-copper(II) charge-transfer transitions in the 350–400 nm region, which are absent in the free ligands.

Both the complexes were studied by variable-temperature magnetic susceptibility measurements. Complexes **1** and **2** exhibit $\mu_{eff}$ values of $2.56 \pm 0.01\ \mu_B$ (per dimer) and $3.67 \pm 0.01\ \mu_B$ (per tetramer), respectively, in the temperature range 5–290 K. The values are expected for magnetically isolated $S$ = 1/2 spin systems [for $d^9$ copper(II) centers], with $g$ = 2.101 and 2.128 for complexes **1** and **2**, respectively. The temperature-independent $\mu_{eff}$ values for the complexes clearly establish the isolated spins without any exchange interaction between the paramagnetic centers. This behavior can be explained by the ligand conformation and also by the presence of $sp^3$ hybridized carbon atoms in the spacer between the coordination sites of the ligands.

### Crystal Structure of 1

The X-ray crystal structure of the neutral complex **1** reveals a dinuclear copper(II) double-stranded helicate with the two heterotopic ligands oriented head-to-head (HH). The coordination polyhedron around each copper ion is best described as square-planar severely distorted to a flattened tetrahedral configuration, in which the metals are coordinated by two phenolate oxygen atoms and two imine nitrogen atoms from the anionic $L^1$ ligands (Figure 1). The Cu–N bonds [range 1.968(8)–1.983(8) Å, Table 1] are slightly longer than the Cu–O bonds [1.858(7)–1.892(8) Å]. These values are within the range usually reported for salicylaldiminato copper complexes.

The chelating ligands form a dihedral angle of 57.4(2)° between planes PhN1–O1 and PhN3–O3 at Cu1 and 44.2(3)° at Cu2 (PhN2–O2/PhN4–O4). Dihedral angles of 0° and 90° would be expected for planar and pseudo-tetrahedral geometries, respectively. Moreover, a different stereochemical orientation of the chelating fragments is observed at the metal ions; the nitrogen (and oxygen) donors are in a pseudo-*trans* arrangement at Cu(1) and *cis* arrangement at Cu(2), which leads to the almost normal orientation of the coordination planes (Figure 1). The separation between the metal ions is 7.687(3) Å. The bis(bidentate) ligand

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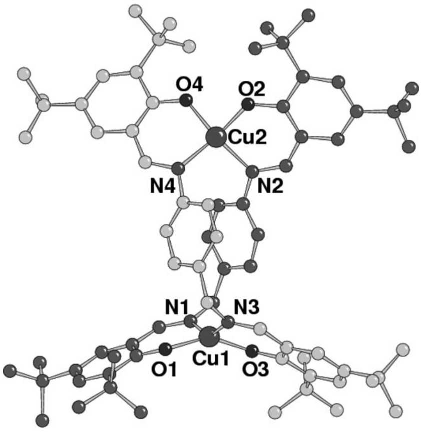

Figure 1. Perspective view of the dinuclear complex **1** highlighting the $C_2$ symmetry.

Table 1. Selected bond lengths [Å] and angles [°] for complex **1**.

| | | | |
|---|---|---|---|
| Cu(1)–O(1) | 1.880(7) | Cu(2)–O(2) | 1.861(9) |
| Cu(1)–O(3) | 1.858(7) | Cu(2)–O(4) | 1.892(8) |
| Cu(1)–N(1) | 1.983(8) | Cu(2)–N(2) | 1.974(10) |
| Cu(1)–N(3) | 1.968(8) | Cu(2)–N(4) | 1.970(10) |
| O(1)–Cu(1)–O(3) | 148.1(3) | O(2)–Cu(2)–O(4) | 88.9(4) |
| O(1)–Cu(1)–N(1) | 93.5(3) | O(2)–Cu(2)–N(2) | 94.3(4) |
| O(1)–Cu(1)–N(3) | 95.6(3) | O(2)–Cu(2)–N(4) | 149.7(4) |
| O(3)–Cu(1)–N(1) | 95.6(3) | O(4)–Cu(2)–N(2) | 149.7(4) |
| O(3)–Cu(1)–N(3) | 93.7(3) | O(4)–Cu(2)–N(4) | 93.2(4) |
| N(1)–Cu(1)–N(3) | 145.9(3) | N(2)–Cu(2)–N(4) | 98.9(4) |
| Cu1–Cu2 | 7.687(3) | | |

strands wrap around the copper centers with a similar relative orientation (HH), which gives rise to a double-helical structure with $C_2$ symmetry, although no crystallographic twofold axis passes through the metal ions. The double helix has a helical twist of ca. 108°, as defined by the Cu1–N1(N3)–N2/(N4)–Cu2 torsional angle. The complex is therefore chiral with a propeller or screw-shaped molecular entity, and the unit cell contains both the configurations, with a centrosymmetric space group.

Interestingly, the complex shows an intramolecular stacking interaction between the central phenyl rings of the two ligand strands with a centroid-to-centroid distance of 3.513(7) Å. These phenyl rings are not parallel but form a dihedral angle of 13.36°. The intramolecular face-to-face π–π interaction stabilizes the double-helical structure of the molecule, which drives the complex to the thermodynamically more stable complex with respect to the head-to-tail configuration arrangement of the ligand strands. This aspect is very peculiar since both structures of the analogous copper complex[58,59] containing the *N*,*N′*-bis(salicylidene)-1,4-phenylenedimethanamine ligand show two independent units with different orientations of the xylylene rings. These rings present a centroid-to-centroid distance of ca. 5.24 Å for the approximately parallel conformation (dihedral angle of 67.6 and 39.7°) and are perpendicular to one another in the second rotational isomer. On the other hand, a weak π–π interaction is present in the helical structure of the $Cu_2$[*N*,*N′*-bis(salicylidene)-1,3-phenylenedimethanamine]$_2$ (4.44 Å),[57] and a double π–π interaction (3.5–3.9 Å) is realized in the Cu complexes containing the longer ligands bis(salicylidene-4,4′-diaminodiphenylmethane)[54] and bis(salicylidene)-4,4′-diaminodiphenylether.[50]

## Crystal Structure of 2

The crystal structure of **2** was determined and the molecular structure is shown in Figure 2. The complex is a $Cu_4(L^2)_4$ neutral assembly with a slightly distorted tetrahedral geometry; the four copper(II) centers are located at the vertices of a tetrahedron with intermetallic distances (between metal ions connected by the ligand $L^2$) in the range 7.288(2)–8.026(3) Å (Table 2). The coordination geometry is significantly distorted from square planar to an extremely flattened tetrahedral configuration and is characterized by coordination bond lengths and angles similar to those observed in complex **1** (Table 2). In fact, each copper(II) center is doubly chelated in a *trans* position by two phenolate oxygen and two imino nitrogen donors; one of the nitrogen atoms is from a HC=N–Ph fragment the other from a HC=N-$(CH_2)_2$-Ph fragment. Each copper(II) center in **2** is bound by donors from each of two different ends of the two ligands. The Cu–N and the Cu–O bond lengths fall in the range 1.936(8)–1.963(7) Å and 1.878(6)–1.918(7) Å, respectively, (Table 2). In each coordination sphere, the iminophenolate ligand planes form a dihedral angle of 52.8(2), 54.4(2), 60.3(2), and 57.7(1)° for the Cu1–Cu4 ions, respectively. Ligands connecting Cu1–Cu2 and Cu3–Cu4 have the same conformation, which is characterized by a torsion angle about the methylene $CH_2$–$CH_2$ bond of ca. –63°; the conformation of the ligands connecting Cu2–Cu3 and Cu1–Cu4 is also *gauche*, but the corresponding torsion angle is of opposite sign (ca. +60°).

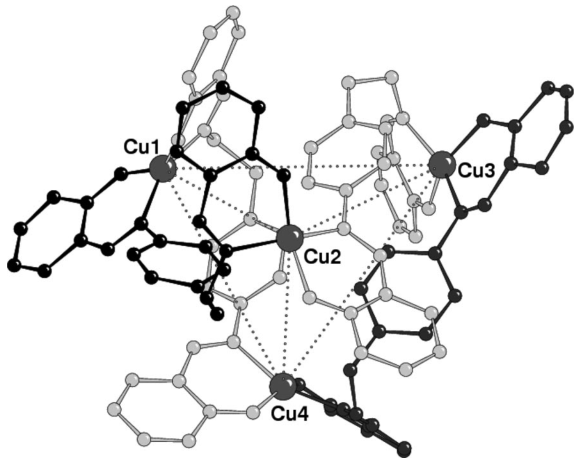

Figure 2. View of the tetranuclear complex **2** (*tert*-butyl groups not shown for clarity).

Here the more flexible ligand $H_2L^2$, characterized by an additional methylene group, leads to a tetranuclear complex, which is stabilized by intramolecular phenyl-ring–metal interactions (Cu1– and Cu3–phenyl 3.9 Å) and by several CH–π interactions (2.75–2.90 Å). No significant in-

Table 2. Selected bond lengths [Å] and angles [°] for complex **2**.

| | | | |
|---|---|---|---|
| Cu(1)–O(1) | 1.915(6) | Cu(3)–O(4) | 1.884(7) |
| Cu(1)–O(8) | 1.904(6) | Cu(3)–O(5) | 1.918(7) |
| Cu(1)–N(1) | 1.955(7) | Cu(3)–N(4) | 1.959(8) |
| Cu(1)–N(8) | 1.946(8) | Cu(3)–N(5) | 1.963(7) |
| Cu(2)–O(2) | 1.878(6) | Cu(4)–O(6) | 1.890(6) |
| Cu(2)–O(3) | 1.905(6) | Cu(4)–O(7) | 1.905(6) |
| Cu(2)–N(2) | 1.936(8) | Cu(4)–N(6) | 1.962(7) |
| Cu(2)–N(3) | 1.957(8) | Cu(4)–N(7) | 1.971(8) |
| O(1)–Cu(1)–O(8) | 148.2(3) | O(4)–Cu(3)–O(5) | 149.4(3) |
| O(1)–Cu(1)–N(1) | 94.4(3) | O(4)–Cu(3)–N(4) | 93.2(3) |
| O(1)–Cu(1)–N(8) | 92.3(3) | O(4)–Cu(3)–N(5) | 92.2(3) |
| O(8)–Cu(1)–N(1) | 91.7(3) | O(5)–Cu(3)–N(4) | 93.6(3) |
| O(8)–Cu(1)–N(8) | 94.0(3) | O(5)–Cu(3)–N(5) | 92.9(3) |
| N(1)–Cu(1)–N(8) | 157.3(3) | N(4)–Cu(3)–N(5) | 157.3(3) |
| O(2)–Cu(2)–O(3) | 150.1(3) | O(6)–Cu(4)–O(7) | 153.1(3) |
| O(2)–Cu(2)–N(2) | 93.5(3) | O(6)–Cu(4)–N(6) | 93.6(3) |
| O(2)–Cu(2)–N(3) | 92.4(3) | O(7)–Cu(4)–N(6) | 93.6(3) |
| O(3)–Cu(2)–N(2) | 93.7(3) | O(6)–Cu(4)–N(7) | 90.8(3) |
| O(3)–Cu(2)–N(3) | 92.9(3) | O(7)–Cu(4)–N(7) | 92.2(3) |
| N(2)–Cu(2)–N(3) | 155.5(3) | N(6)–Cu(4)–N(7) | 158.0(3) |
| Cu(1)–Cu(2) | 8.026(3) | Cu(2)–Cu(3) | 7.644(2) |
| Cu(1)–Cu(4) | 7.288(2) | Cu(3)–Cu(4) | 7.992(2) |
| Cu(1)···Cu(3) | 8.239(2) | Cu(2)···Cu(4) | 7.667(2) |

tra- or intermolecular π–π interactions are operative among the aromatic rings; the shortest distance between two phenyl ring centroids is ca. 4.4 Å inside the tetranuclear complex.

It is interesting to observe that the metal ions describe an almost regular tetrahedron. The distances between the nonconnected metals Cu(1) and Cu(3), and Cu(2) and Cu(4) are 8.239(2) and 7.667(2) Å, respectively, and are thus comparable to those measured between the ligand spacers. When viewed normally to the Cu(1)–Cu(3) and Cu(2)–Cu(4) vectors (Figure 3), the complex exhibits a small cavity, although its dimensions do not allow the insertion of any chemical species.

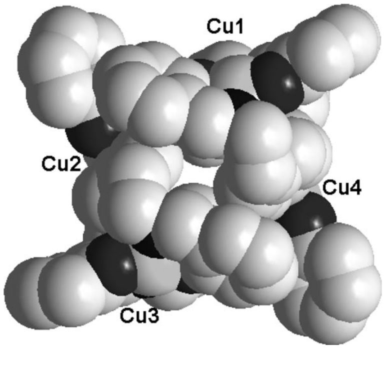

Figure 3. Space-filling representation of complex **2** showing the inside cavity (H atoms and *tert*-butyl groups omitted).

As a comparison we also performed the X-ray structural analysis of $H_2L^2$. The molecular structure of the free ligand is disordered, and the molecule is located on a center of symmetry (Figure 4). However, the ligand clearly adopts an *anti* conformation about the $–CH_2–CH_2–$ bond [torsion angle N(1′)–C(15)–C(14)–C(11) of 179.7(3)°], in contrast to the conformation assumed on coordination in **2**. The PhN(1)–O(1) moiety forms a dihedral angle of 37.8(1)° with the central phenyl ring, and a strong intramolecular H-bond is operative between the OH and N atom (N···O distance of 2.590 Å).

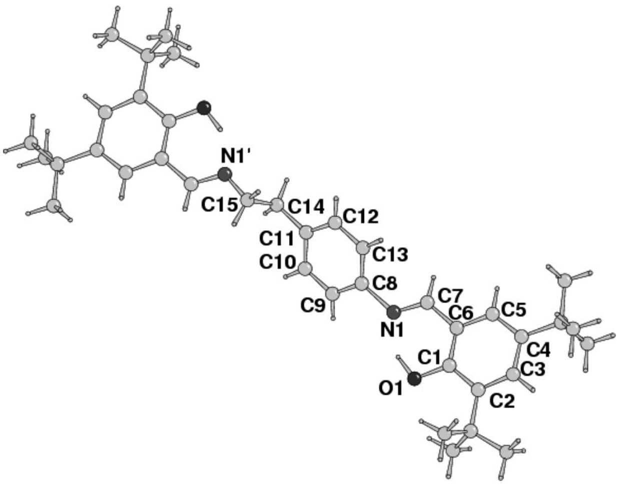

Figure 4. Molecular structure of ligand $H_2L^2$. The molecule is located on a center of symmetry with the central $CH_2–CH_2–Ph$ moiety disordered over two positions (only one orientation is shown for clarity).

Tetranuclear copper(II) complexes containing bis(N,O-bidentate) Schiff base ligands were also reported by Yoshida et al.[50,56] These complexes are stabilized by weak aromatic π–π and CH–π interactions and present almost coplanar metals in a rectangular arrangement. Here, the use of bis(chelating) flexible ligands, which should favor the formation of dinuclear helicate structures,[50,54,58] leads to a globular tetranuclear species instead. The solvent mixture (thf and acetonitrile) used for crystallization of **2** may have a template effect on the nuclearity of the complex. Unfortunately, the use of a dichloromethane/methanol solvent mixture did not yield good quality crystals of **2** for single-crystal diffraction.

## Conclusions

Here we present a system in which the same metal ion and two iminophenol Schiff base ligands with asymmetric spacers give rise to complexes of different nuclearity. We discuss the factors that favor the formation of a given complex. In the dinuclear double-helical complex, it is the intramolecular π–π stacking interaction that stabilizes the complex, which compromises the flattened tetrahedral geometry of the copper(II) ions. The conformation preference of the ligand in this case dominates the geometrical preference of the metal ion. On the other hand, the tetranuclear assembly is stabilized as a result of the flexible nature of the ligand. The formation of a dinuclear assembly, on the basis of ligand conformation/metal geometry or other noncovalent interactions, is not feasible in this case. The results described herein indicate that not only the geometry of the metal ion but also the conformation of the ligand and/or other intermolecular interactions play a fundamental role in directing the self-assembled supramolecular architecture.

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The general effect of varying the asymmetric ligand spacer on the supramolecular architecture is now under further investigation.

## Experimental Section

Commercial grade chemicals were used for the synthesis, and solvents were distilled and dried before use.

**General Method for the Synthesis of Ligands:** To a solution of 2,4-di-*tert*-butyl salicylaldehyde (1.68 g, 7.2 mmol) in dry ethanol (in 40 mL) was added the corresponding amine (3.6 mmol) in a dropwise manner at room temperature while constantly stirring. The yellow solution was further stirred for 3 d at room temperature, after which a yellow solid precipitated. The solid was isolated by filtration and dried in air. The crude product was recrystallized from dichloromethane/methanol (1:1) solvent mixture.

**Ligand $H_2L^1$:** Yield: 1.7 g (83%). $C_{37}H_{50}N_2O_2$ (554.39): calcd. C 80.10, H 9.08, N 5.05; found C 80.1, H 9.1, N 5.3. IR (KBr): $\tilde{\nu}$ = 3437 (br.), 2959–2868 (s), 1622 (s), 1587 (s), 1468–1441 (s), 1250, 1171, 829 (m) $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 13.69 (s, 2 H, phenol OH), 8.65 (s, 1 H, imine C–H), 8.47 (s, 1 H, imine C–H), 7.45 (d, $J$ = 2.1 Hz, 1 H), 7.40 (d, $J$ = 2.1 Hz, 1 H), 7.38 (s, 1 H, aromatic), 7.35 (s, 1 H, aromatic), 7.30 (s, 1 H, aromatic),7.27 (s, 1 H, aromatic), 7.22 (d, $J$ = 2.4 Hz, 1 H), 7.12 (d, $J$ = 2.3 Hz, 1 H), 4.81 (s, 2 H, $-CH_2-$), 1.48 (s, 9 H, *tert*-butyl), 1.44 (s, 9 H, *tert*-butyl), 1.33 (s, 9 H, *tert*-butyl), 1.31 (s, 9 H, *tert*-butyl) ppm. ESI-MS (positive ion mode, dichloromethane): *m*/*z* (%) = 555.42 (100) $[H_2L^1 + H]^+$, 339.27 (20) $[(H_2L^1$ – 2,4-di-*tert*-butylsalicylaldehyde) $+ H]^+$. UV/Vis (dichloromethane): $\lambda$ ($\varepsilon$, $M^{-1}cm^{-1}$) = 350 (sh.), 327 (sh.), 313 (2850), 271 (3520) nm.

**Ligand $H_2L^2$:** Yield: 1.45 g (71%). X-ray quality crystals were grown from a solvent mixture of dichloromethane and acetonitrile (1:1). $C_{38}H_{52}N_2O_2$ (568.82): calcd. C 80.24, H 9.21, N 4.92; found C 80.1, H 9.3, N 5.1. IR (KBr): $\tilde{\nu}$ = 3443 (br.), 2955–2866 (s), 1633–1620 (s), 1585 (s), 1471–1435 (s), 1250, 1167, 825 (m) $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 13.80 (s, 1 H, phenolic OH), 13.75 (s, 1 H, phenolic OH), 8.64 (s, 1 H, imine C–H), 8.29 (s, 1 H, imine C–H), 7.45 (d, $J$ = 2.0 Hz, 1 H), 7.39 (d, $J$ = 2.1 Hz, 1 H), 7.29–7.22 (m, 5 H, aromatic), 7.05 (d, $J$ = 2.2 Hz, 1 H), 3.85 (t, 2 H, $-CH_2-$), 3.05 (t, 2 H, $-CH_2-$), 1.49 (s, 9 H, *tert*-butyl), 1.47 (s, 9 H, *tert*-butyl), 1.34 (s, 9 H, *tert*-butyl), 1.31 (s, 9 H, *tert*-butyl) ppm. ESI-MS (positive ion mode, dichloromethane): *m*/*z* (%) = 569.36 (100) $[H_2L^2 + H]^+$. UV/Vis (dichloromethane): $\lambda$ ($\varepsilon$, $M^{-1}cm^{-1}$) = 357 (sh.), 328 (2330), 313 (sh.), 270 (2660) nm.

**General Method for the Synthesis of Copper(II) Complexes:** To a suspension of ligand (2.0 mmol) in acetonitrile (25 mL), triethylamine (0.55 mL, 4 mmol) was added. To that suspension, an acetonitrile solution (5 mL) of $CuCl_2\cdot 2H_2O$ (0.36 g, 2.12 mmol) was added slowly at room temperature while stirring. The solution immediately turned brown and was allowed to stir for 24 h. The precipitated brown solid was isolated by filtration, washed with acetonitrile, and dried. The crude solid obtained was then recrystallized from a solvent mixture of dichloromethane and acetonitrile.

**Complex 1:** X-ray quality single crystals were grown from a dichloromethane/methanol solvent mixture. Yield: 1.04 g (84.4%). $C_{74}H_{96}Cu_2N_4O_4$ (1232.63): calcd. C 72.10, H 7.85, N 4.55; found C 71.7, H 7.9, N 4.8. IR (KBr): $\tilde{\nu}$ = 3431 (br.), 2955–2868 (s), 1616 (s), 1585 (s), 1529 (s), 1431 (s), 1255, 1169 (s), 837 $cm^{-1}$. ESI-MS (positive ion mode, acetonitrile): *m*/*z* (%) = 1231.06 (30) $[Cu_2L^1{}_2]^+$, 615.18 (100) $[CuL^1]^+$. UV/Vis (dichloromethane): $\lambda$ ($\varepsilon$, $M^{-1}cm^{-1}$) = 674 (930), 433 (sh.), 398 (28450), 296 (65200) nm.

**Complex 2:** X-ray quality single crystals were grown from a thf/acetonitrile solvent mixture. Yield: 0.94 g (74.6%). $C_{152}H_{200}Cu_4N_8O_8$ (2521.36): calcd. C 72.40, H 7.99, N 4.44; found C 72.5, H 7.9, N 4.5. IR (KBr): $\tilde{\nu}$ = 2955–2868 (s), 1616 (s), 1591 (s), 1529 (s), 1433 (s), 1257, 1169 (s), 835 $cm^{-1}$. ESI-MS (positive ion mode, acetonitrile): *m*/*z* (%) = 1887.69 (10) $[Cu_3L^2{}_3]^+$, 1261.11 (20) $[Cu_2(HL^2)_2]^+$, 630.23 (80) $[Cu(HL^2)]^+$, 569.33 (100)

Table 3. Crystallographic data of complexes **1**, **2**, and ligand $H_2L^2$.

| | **1** | **2** | $H_2L^2$ |
|---|---|---|---|
| Empirical formula | $C_{74}H_{96}Cu_2N_4O_4$ | $C_{152}H_{200}Cu_4N_8O_8$ | $C_{38}H_{52}N_2O_2$ |
| Formula weight | 1232.63 | 2521.36 | 568.82 |
| Crystal system | triclinic | monoclinic | monoclinic |
| Space group | $P\bar{1}$ | $I2/a$ | $P2_1/n$ |
| $a$ [Å] | 10.716(4) | 34.258(5) | 8.261(3) |
| $b$ [Å] | 11.656(3) | 20.099(4) | 20.156(4) |
| $c$ [Å] | 33.275(8) | 52.269(14) | 10.332(4) |
| $\alpha$ [°] | 87.57(4) | – | – |
| $\beta$ [°] | 87.76(3) | 94.777(19) | 97.83(3) |
| $\gamma$ [°] | 73.50(6) | – | – |
| Volume [Å$^3$] | 3980(2) | 35865(13) | 1704.3(10) |
| $Z$ | 2 | 8 | 2 |
| $D_{calcd.}$ [Mg/m$^3$] | 1.029 | 0.934 | 1.108 |
| $\mu$ Mo-$K_\alpha$ [mm$^{-1}$] | 0.577 | 0.513 | 0.067 |
| $F$(000) | 1316 | 10784 | 620 |
| $\theta$ range data collection [°] | 1.82–22.54 | 0.78–21.13 | 2.02–27.73 |
| Reflections collected | 21529 | 59529 | 18706 |
| Unique reflections | 10297 | 19377 | 3950 |
| $R$(int) | 0.1043 | 0.1357 | 0.0394 |
| Data [$I > 2\sigma(I)$] | 5390 | 7332 | 2827 |
| Parameters refined | 758 | 826 | 253 |
| Goodness-of-fit on $F^2$ | 1.157 | 0.871 | 1.034 |
| $R_1$ [$I > 2\sigma(I)$] | 0.0963 | 0.0861 | 0.0531 |
| $wR_2$ | 0.2317 | 0.2130 | 0.1282 |
| Residuals [e Å$^{-3}$] | 0.933, –1.299 | 0.685, –0.454 | 0.341, –0.199 |

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$[H_2L^2+H]^+$. UV/Vis (acetonitrile): $\lambda$ ($\varepsilon$, $\text{M}^{-1}\,\text{cm}^{-1}$) = 664 (997), 401 (54000), 308 (sh.), 282 (114400) nm.

**Physical Methods:** Fourier transform infrared spectroscopy on KBr pellets was performed on a Shimadzu FT-IR 8400S instrument. Elemental analyses were performed on a Perkin–Elmer 2400 series II CHN series. Solution electronic spectra were measured on an Agilent 8453 diode array spectrophotometer. Electrospray mass spectra were recorded with a Waters QTOF Micro YA263 instrument. Magnetic susceptibilities of the polycrystalline samples were recorded on a SQUID magnetometer (MPMS, Quantum Design) in the temperature range 2–290 K with an applied field of 1 T. Diamagnetic contributions were estimated for each compound by using Pascal's constants. $^1$H NMR spectra were measured by using a Bruker DPX-300 spectrometer.

**X-ray Crystallographic Data Collection and Refinement of the Structures:** Crystallographic data for **1**, **2**, and the ligand $H_2L^2$ are summarized in Table 3. Diffraction data were collected at 150(2) K (for **1** and **2**) and at 100(2) K for ligand $H_2L^2$ on a Bruker Smart APEX II diffractometer (Mo-$K_\alpha$ radiation, $\lambda$ = 0.71073 Å). Cell refinement, and indexing and scaling of the data set were carried out by using the Apex2 v2.1-0 software.[60] The structure was solved by direct methods and subsequent Fourier analyses and refined by the full-matrix least-squares method based on $F^2$ with all observed reflections.[61] One of the ligands in **2** was found to be statistically disordered over two positions (0.52/0.48 occupancies), and its parameters were refined with geometrical restraints. Crystals **1** and **2** diffract at low angle (21–22°) and reveal high potential solvent area volume (23.1% in **1** and 27.9% in **2**), but any attempt to model solvent molecules were unsuccessful and led to high R factors, as reported in Table 3. The ligand $H_2L^2$ was found to be disordered about an inversion centre, and the atoms of the $CH_2$–$CH_2$–Ph group were isotropically refined. H atoms were located at calculated positions. All the calculations were performed by using the WinGX System, Ver 1.70.01.[62] CCDC-686326, -686327, and -686328 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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