



Synthesis of New Tetradentate H₂salophen Ligands and Their Copper (II) Complexes

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In Loving Memory of Late Professor Doctor "Mohamed Refaat Hussein Mahran"

Abstract

A synthesizing metal salophen complex is extremely significant owing to their wide variety of potential applications, particularly in catalysis, optical limiting materials, and pharmaceutical purposes. The present work aims to design and synthesis a series of copper salophen complexes associated with the diazo moiety according to the adapted strategy in two straight and effective steps. Salophen-type ligands containing tetradentate Schiff's base **H₂L** were synthesized by a regular condensation reaction of azo-based salicylaldehyde derivatives (two equivalents) with *o*-phenylenediamine (one equivalent) in refluxing dioxane. Consequently, the previous salophen-type ligands reacted with copper chloride dihydrate to generate the corresponding copper (II) salphen complexes. The synthesized tetradentate ligands and their copper salophen complexes were characterized with elemental analysis and spectroscopic techniques, showing that the coordination of the ligands with copper ions took place through the ONNO donor sites of two azomethine-N and two deprotonated phenolic-OH donors, suggesting the complex's general formula as **CuL**. The thermogravimetric analysis and molar conductivity results are in good agreement with the expected structures.

Keywords: H₂salophen; Schiff's bases; Tetradentate ligands; Diazo; Copper salophen complexes.

1. Introduction

The transition metal complexes of Schiff base have been of considerable and remarkable interest with several applications owing to their unique properties, such as their stability in homogeneous or heterogeneous catalysts, inducing chirality substrates, and their potential biological activities.^[1-7] In this regard, copper-based complexes illustrated promising prospects due to their low-cost synthesis and enormous applications.^[8-10] It was reported, copper (II) complexes containing BIAN ligands exhibited characteristic catalytic activity during the oxidation process of alkane and alcohol with peroxides.^[11] Additionally, phosphole-copper (I) complexes showed catalytic performance in the synthesis of triazole derivatives through a three-component reaction.^[12] Biologically speaking, copper (II) complexes bearing non-steroidal anti-inflammatory drugs demonstrated noteworthy antioxidant activity via intercalation with calf-thymus DNA.^[13] On the other hand, azo derivatives are widely employed in different

applications.^[14,15] The azo group has the ability to alter the molecular confirmation shape *via* reversible isomerization (cis/trans), it is viewed as the most important chromophoric group in dye manufacturing.^[16,17] Furthermore, azo compounds were reported as antitumor, antifungal, antiviral, and antibacterial agents.^[18-23] Accordingly, combining diazo or Schiff base groups with copper complexes plays a crucial role in several fields.^[24,25] Copper complexes containing Schiff-bases were employed as catalysts in synthesis triazole derivatives through the azide-alkyne cycloaddition reaction.^[26] Moreover, copper complexes containing azo multifunctional ligands were synthesized and evaluated against Alzheimer's disease, showing encouraging data compared to the Donepezil drug.^[27] Furthermore, copper complexes of azo-based ligands were tested experimentally and theoretically as drug-like molecules, presenting a characteristic binding behaviour with nucleic acids.^[28] In this context, metal-salophen (salicylidene-*o*-phenylenediamine)

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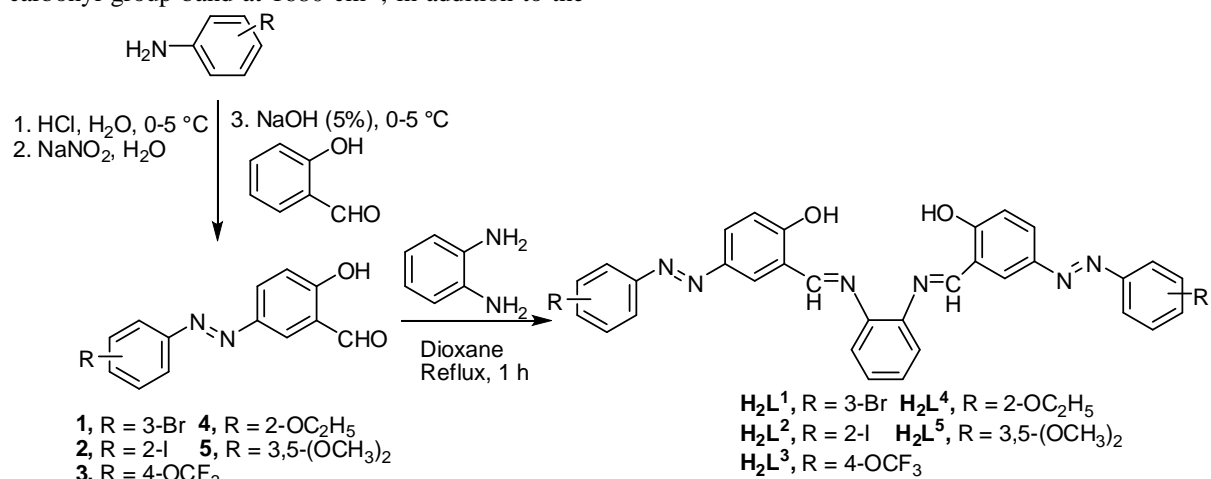
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complexes are extremely stable complexes with extensive applications in several fields, including catalysis,^[29] optical limiting^[30] and medicinal chemistry.^[31-33] Chromium (III) salophen complexes exhibited promising co-catalytic activity in synthesizing styrene carbonate through the cycloaddition of CO₂ on the styrene epoxide.^[34] Moreover, cobalt (III) salophen complexes were synthesized and evaluated against lung cancer, showing promising results for cancer therapy.^[35]

Considering the aforementioned applications, it is crystal clear that integration of Schiff's bases and diazo groups in salophen complexes is regarded as a promising pathway, whatever the applications targeted. Here, we aim to design and synthesize H₂salophen-type ligands containing diazo and Schiff's base moieties and study their metal complexation with copper (II) chloride dihydrate.

Results and discussion

The 5-(aryldiazo)salicylaldehyde precursors 1-5 were synthesized through the coupling reaction of salicylaldehyde with aryldiazonium chloride derivatives, prepared *in situ* (Scheme 1). Depending on the resonance effects of formyl and hydroxyl groups in salicylaldehyde, the coupling orientation is directed to position 5, which is *meta* to the formyl and *para* to the hydroxyl groups, producing 5-(aryldiazo)salicylaldehyde precursors 1-5 as a clean-cut products.^[20] This is in accordance with Hammett σ constants, where position 5 at salicylaldehyde is the more electron-rich site. The IR spectrum of 5-(2-iodophenyldiazo)-salicylaldehyde 2 showed a carbonyl group band at 1680 cm⁻¹, in addition to the



Scheme 1: Synthesis of the H₂salophen-type tetradentate ligands

Due to the successful preparation of H₂salophen-type ligands H₂L¹⁻⁵, it was encouraged to investigate their complexation behaviour towards the copper cation, aiming to synthesize copper salophen complexes,

hydroxyl band at 3322 cm⁻¹. Regarding the ¹H NMR spectrum, there are two characterized signals at 10.12 and 11.47 ppm, which corresponded to the formyl and hydroxyl protons, respectively. Further, a complex multiplet of peaks at 6.80-7.90 ppm is typical for the aromatic protons. Concerning the ¹³C NMR spectrum, provided strong evidence for this interpretation. Besides the aromatic carbons in the expected regions, 117.3-164.3 ppm, two diagnostic signals for C-I and formyl carbons at: 102.6 and 196.6 ppm, respectively.

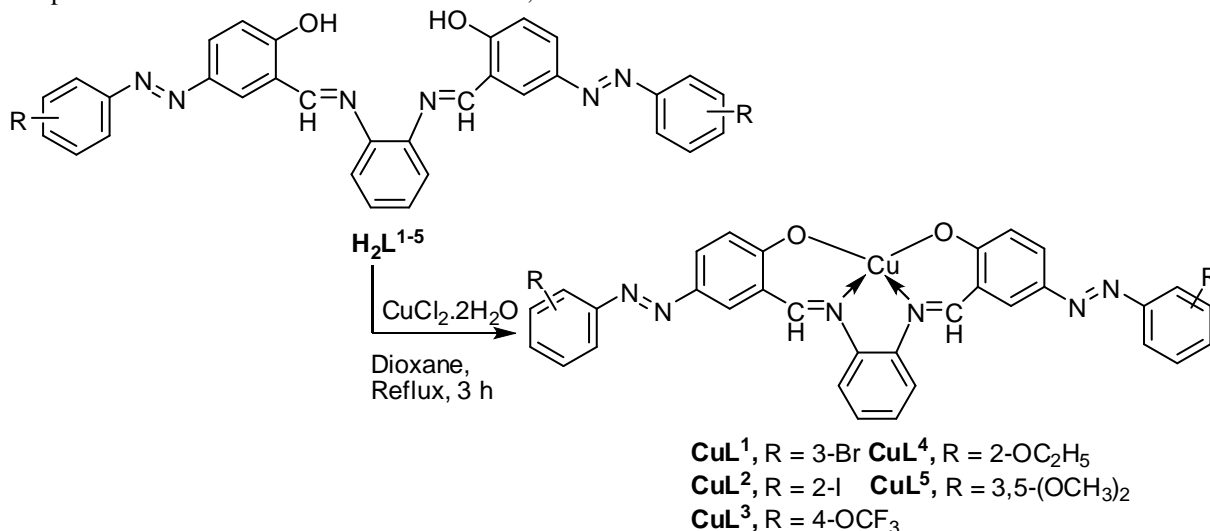
H₂salophen-type Schiff's base ligands H₂L¹⁻⁵ were synthesized through the interaction of two moles of salicylaldehydes 1-5 with one mole of *o*-phenylenediamine in refluxing dioxane. Their structural assignment was secured *via* spectroscopic and microanalytical methods. Generally, the IR spectra of H₂L¹⁻⁵ revealed the disappearance of the carbonyl group band, beside the existing bands in the 1613-1619 cm⁻¹ region for the azomethine group. Moreover, characteristic bands at 3410-3447 cm⁻¹ for the hydroxyl groups. The ¹H NMR spectra showed signals around 13.7 and 9.14 ppm, related to OH and azomethine protons, respectively. Moreover, all the aromatic protons were observed in the expected regions. H₂L⁴, for example, the ¹H NMR spectrum indicated two distinct signals for ethoxy protons at 1.39 (triplet) and 4.22 (quartet) ppm, respectively. Additionally, two characterized signals for azomethine and hydroxyl protons at 9.13 and 13.66 ppm, respectively. Further elucidation for H₂salophen-type ligand structure came from mass spectra, showing molecular ion peaks in agreement with their molecular formula. For instance, H₂L¹ displayed a molecular ion peak at 682.

CuL¹⁻⁵. Thus, when an ethanolic solution of one equivalent of copper chloride dihydrate was added to a stirred and refluxed solution of one equivalent of H₂L¹⁻⁵ in dioxane, the corresponding copper salophen complexes CuL¹⁻⁵, were generated in quantity yields,

as depicted in Scheme 2. The copper (II) ions are coordinated to two nitrogen atoms from the imine moieties and two oxygen atoms of the phenolic parts.^[3,36]

Elemental analysis:

For copper analysis, the decomposition of the copper complexes CuL¹⁻⁵ was occurred with nitric acid, and



Scheme 2: Proposed structure of the copper salophen complexes

The infrared spectral data:

To confirm the binding mode between the H₂salophen-type ligands and the copper ion, the IR spectra of the ligands H₂L¹⁻⁵ were compared with the corresponding copper salophen complexes CuL¹⁻⁵. Regarding H₂L¹⁻⁵, strong bands appeared at 1615 cm⁻¹; assigned to the stretching vibration of the azomethine group (C=N). On the other hand, the stretching vibrations of the azomethine group of copper salophen complexes CuL¹⁻⁵, were shifted to higher wave numbers by 7-20 cm⁻¹, elucidating the coordination of the azomethine-nitrogen to copper ion. Moreover, phenolic C-O stretching vibrations were recorded at 1280 cm⁻¹, in the case of the ligands H₂L¹⁻⁵. Whereas, the vibrations of the phenolic C-O of copper salophen complexes CuL¹⁻⁵ was shifted to a higher frequency, recording 1384-1431 cm⁻¹, confirming the coordination of the phenolic oxygen atom with the copper ion. Additionally, copper salophen complexes IR spectra showed bands in the region 408-445 cm⁻¹, recorded to $\nu(\text{Cu-phenolic O})$, and other bands in the region 502-542 cm⁻¹, corresponded to $\nu(\text{Cu-N})$.

The electronic absorption (UV-vis) spectra:

The electronic absorption spectra were measured in DMF. Regarding H₂salophen-type ligands, there are two main absorption bands at 340 and 460 nm. The first peak, 340 nm regions for the $\pi \rightarrow \pi^*$ electron transition of aromatic C=C bonds. The second band

the solution was diluted to be suitable for atomic absorption analysis. The elemental analysis of the copper complexes CuL¹⁻⁵ revealed the absence of chlorine atoms, which is in complete agreement with the suggested copper salophen complex structure, with the general formula CuL.

(460 nm) was a probable assignment for $n \rightarrow \pi^*$ transition for the azomethine function moiety. On the other hand, copper salophen complexes spectra showed absorption bands at 400 nm regions, low-intensity heap bands, which were recorded to the transition of azomethine chromophore $\rightarrow \pi^*$. The shifts in the transition of azomethine chromophore $\rightarrow \pi^*$ bands confirmed the coordination of the azomethine nitrogen atom with the copper ion.

Molar conductivity:

Conductivity measurement was utilized to prove the metal salophen complexes, during the ionization of the complexes. Solutions of 10⁻³ M copper complexes in DMF were measured. The negligible values of molar conductance (4.6-5.7 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) indicated the non-electrolyte and non-ionized natures of copper complexes, which confirm the deprotonation of phenolic OH through bonding as an oxygen anion with a copper ion.

The thermogravimetric analysis (TGA):

In order to obtain more confirmation for copper salophen complex structure CuL¹⁻⁵ and to study their thermal stability, the thermogravimetric (TGA) and differential thermogravimetric (DTG) analysis were carried out at temperatures up to 1000 °C. Generally, the copper compounds have similar TGA thermograms, revealing two thermal steps. A TGA thermogram of CuL⁴ as a representative example was discussed. The thermogravimetric curve obtained with

CuL^4 was decomposed thermally through two decomposition steps. Within the temperature range of 250-310 °C, the first step took place with a mass loss of 13.8%, suggesting the elimination of two ethoxy groups (calculated at 13.3%). The DTG curve revealed an exothermic peak at 276 °C. Furthermore, within the temperature range of 310-486 °C, the second step occurred with a mass loss of 79.3%, representing the complete decomposition of the remaining organic component (calculated at 79.8%). The DTG curve claimed an exothermic peak at 417 °C. Finally, the remaining 11.3% was related to CuO .

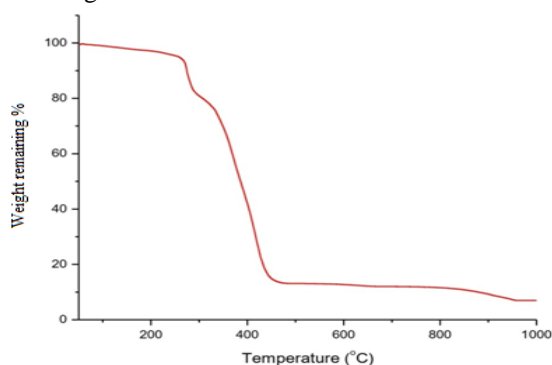


Fig. 1: TGA of CuL^4

Conclusion

Schiff base and diazo moieties were integrated into novel $\text{H}_2\text{salophen}$ -type ligands H_2L^{1-5} via a condensation reaction between azo-based salicylaldehyde derivatives and *o*-phenylenediamine. The $\text{H}_2\text{salophen}$ -based Schiff's base ligands were subjected to a metallation process with copper chloride dihydrate, generating the corresponding copper salophen complexes. The ligands and their copper complexes were verified with elemental analysis and spectroscopic methods (NMR, FT-IR, UV-Vis, and mass spectroscopy). These methods proved that $\text{H}_2\text{salophen}$ -type ligands acted as a tetradentate ligand and coordinated to the central copper (II) ions through the ONNO chelating system, two oxygen (deprotonated phenolic-OH) and two imino nitrogen. Therefore, the composition of the generated copper salophen complexes could be represented as CuL . The thermogravimetric analysis revealed that copper salophen complexes decomposed in two steps, showing weight losses consistent with the theoretical values. Moreover, the molar conductivity in the DMF solution confirmed the non-electrolytic nature of the targeted copper salophen complexes.

Experimental section

NMR spectra were measured on a Bruker instrument at 500 MHz. Infrared spectra were measured using a jascospectrometer. Using DMF, UV spectra were recorded with Shimadzo UV-2401UV-VIS

Spectrophotometer. Perkin-Elmer 2400 analyzer was used to check the elemental analysis.

Synthesis of 2-hydroxy-5-((2-iodophenyl)diazenyl)benzaldehyde (2)

A cold aqueous solution (10 mL) of NaNO_2 (60 mmol) was added to a cold acidic aqueous solution (16 mL conc. HCl and 60 mL water) of 2-Iodoaniline (54 mmol) to give a 2-iodoaniline diazonium chloride solution, which was shaken well and kept at a temperature less than 10 °C. Salicylaldehyde (54 mmol) was dissolved in a 5% NaOH solution (90 mL) and cooled to 0-5 °C. The cooled diazonium chloride solution was added slowly, under stirring, to the cooled salicylaldehyde salt solution. After addition, keep the reaction mixture under a stirring and ice-bath system for 30 min. The desired diazo-based aldehyde 2 was precipitated, filtered, and crystallized from methanol. Yield 92 %; IR: ν/cm^{-1} : 3322 (OH), 1680 (C=O); ^1H NMR (500 MHz, CDCl_3): δ = 7.21 (d, 1H, J = 8.7 Hz, Ar-H), 7.24 (t, 1H, Ar-H), 7.50 (t, 1H, Ar-H), 7.70 (dd, 1H, J = 8.0, 1.5 Hz, Ar-H), 8.10 (dd, 1H, J = 7.9, 1.2 Hz, Ar-H), 8.30 (d, 1H, J = 2.5 Hz, Ar-H), 8.32 (m, 1H, Ar-H), 10.12 (s, 1H, CHO), 11.47 (br, 1H, OH); ^{13}C NMR (126 MHz, CDCl_3): δ = 102.6, 117.3, 118.8, 120.3, 129.0, 130.5, 131.0, 132.3, 140.0, 145.8, 151.0, 164.3, 196.6 (CHO); Anal Calcd for $\text{C}_{13}\text{H}_9\text{IN}_2\text{O}_2$ (352.13): C, 44.34; H, 2.58; N, 7.96; Found: C, 44.21; H, 2.61; N, 7.87%.

Synthesis of 5-(aryldiazo) salicylaldehyde derivatives 1, 3, 4 and 5 see references 1-3.

Synthesis of H_2 Salophen-type tetradentate ligands H_2L^{1-5}

A mixture of *o*-phenylenediamine (1.5 mmol) and 5-(aryldiazo) salicylaldehyde derivatives 1-5 (3 mmol) was refluxed for one hour in dioxane (60 mL). The obtained solid products were filtrated and recrystallized from dioxane to afford the ligands H_2L^{1-5} .

2,2'-{Benzene-*o*-diylbis[nitrilomethylylidene]}bis(4-((*m*-bromophenyl)diazenyl)phenol) (H_2L^1):

Yield: 88 %; IR (KBr, cm^{-1}): 1613 (C=N), 1285 (C-O); ^1H NMR: δ/ppm = 6.94 - 7.98 (m, 16H, Ar-H), 8.73 (s, 2H, Ar-H), 9.13 (s, 2H, CH=N), 13.66 (br, 2H, OH, D_2O exchangeable); MS (m/z , (relative abundance, %)): 682 (M^+ , 22.1); UV-Vis (DMF) ($\lambda_{\text{max}}/\text{nm}$): 349, 469; Anal. Calcd. for $\text{C}_{32}\text{H}_{22}\text{Br}_2\text{N}_6\text{O}_2$ (682.36): C, 56.33; H, 3.25; N, 12.32. Found: C, 56.28; H, 3.11; N, 12.24%

2,2'-{Benzene-*o*-diylbis[nitrilomethylylidene]}bis(4-((*o*-iodophenyl)diazenyl)phenol) (H_2L^2): Yield: 85 %; IR (KBr, cm^{-1}): 1614 (C=N), 1285 (C-O); ^1H NMR: δ/ppm = 6.94 - 7.98 (m, 16H, Ar-H), 8.73 (s, 2H, Ar-

H), 9.13 (s, 2H, CH=N), 13.66 (br, 2H, OH, D₂O exchangeable); MS (*m/z*, (relative abundance,%)): 776 (*M*⁺, 34.3); UV-Vis (DMF) (λ_{max} / nm): 349, 469; Anal. Calcd. for C₃₂H₂₂I₂N₆O₂ (776.37): C, 49.51; H, 2.86; N, 10.82; Found: C, 49.37; H, 2.83; N, 10.67%

2,2'-{Benzene-*o*-diylbis[nitrilomethylidene]}bis(4-((*p*-trifluoromethoxy)phenyl)diazanyl)phenol (*H*₂L³): Yield: 91%; m.p. 220-222 °C; IR (KBr, cm⁻¹): 1615 (C=N), 1277 (C-O); ¹H NMR: δ /ppm = 7.10 - 8.11 (m, 16H, Ar-H), 8.38 (s, 2H, Ar-H), 9.14 (s, 2H, CH=N), 13.70 (br, 2H, OH, D₂O exchangeable); MS (*m/z*, (relative abundance, %)): 692 (*M*⁺; 17.3). UV-Vis (DMF) (λ_{max} / nm): 343, 463; Anal. Calcd. for C₃₄H₂₂F₆N₆O₄ (692.57): C, 58.96; H, 3.20; N, 12.13. Found: C, 58.88; H, 3.14; N, 12.22%

2,2'-{Benzene-*o*-diylbis[nitrilomethylidene]}bis(4-((*o*-ethoxyphenyl)diazanyl)phenol) (*H*₂L⁴): Yield: 94%; m.p. 245-247 °C; IR (KBr, cm⁻¹): 1619 (C=N), 1284 (C-O); ¹H NMR: δ /ppm = 1.39 (t, 6H, *J* = 6.86 Hz, 2CH₂CH₃), 4.22 (q, 4H, *J* = 6.86 Hz, 2CH₂CH₃), 6.80 - 7.98 (m, 16H, Ar-H), 8.73 (s, 2H, Ar-H), 9.13 (s, 2H, CH=N), 13.66 (br, 2H, OH, D₂O exchangeable); MS (*m/z*, (relative abundance, %)): 612 (*M*⁺; 14.4); UV-Vis (DMF) (λ_{max} / nm): 344, 469; Anal. Calcd. for C₃₆H₃₂N₆O₄ (612.68): C, 70.57; H, 5.26; N, 13.72. Found: C, 70.60, H, 5.14, N, 13.60%

2,2'-{Benzene-*o*-diylbis[nitrilomethylidene]}bis(4-((3,5-dimethoxyphenyl)diazanyl)phenol) (*H*₂L⁵): Yield: 93%; IR (KBr, cm⁻¹): 1618 (C=N), 1281 (C-O); ¹H NMR: δ /ppm = 3.79 (s, 12H, 4OCH₃), 7.07 - 8.40 (m, 14H, Ar-H), 8.77 (s, 2H, Ar-H), 9.51 (s, 2H, CH=N), 13.64 (br, 2H, OH, D₂O exchangeable); MS (*m/z*, (relative abundance,%)): 644 (*M*⁺; 34.1); UV-Vis (DMF) (λ_{max} /nm): 351, 463; Anal. Calcd. for C₃₆H₃₂N₆O₆ (644.68): C, 67.07; H, 5.00; N, 13.04. Found: C, 67.12; H 5.14; N, 13.17%

General procedure for the synthesis of copper salophen complexes CuL¹⁻⁵

The CuCl₂.2H₂O (1 mmol) was dissolved in ethanol (a minimum amount) and added drop-wise to a refluxing solution of the ligands H₂L¹⁻⁵ (1 mmol) in dioxane (50 mL). The reaction mixture was refluxed for 3 hours. The generated precipitate was separated by filtration and washed with cold ethanol.

2,2'-{Benzene-*o*-diylbis[nitrilomethylidene]}bis(4-((*m*-bromophenyl)diazanyl)phenoxy) copper complex (*CuL*¹): Yield: 75%; IR (KBr, cm⁻¹): 1600 (C=N), 1392 (C-O), 508 (Cu-O), 430 (Cu-N); Anal. Calcd. for C₃₂H₂₀Br₂CuN₆O₂: C, 51.67; H, 2.71; Cu, 8.54; N, 11.30. Found: C, 51.44, H, 2.64, Cu, 8.42; N, 11.12%; UV-Vis (DMF) (λ_{max} /nm): 401.

2,2'-{Benzene-*o*-diylbis[nitrilomethylidene]}bis(4-((*o*-iodophenyl)diazanyl)phenoxy) copper complex (*CuL*²): Yield: 75%; IR (KBr, cm⁻¹): 1604 (C=N), 504 (Cu-O), 432 (Cu-N); Anal. Calcd. for C₃₂H₂₀CuI₂N₆O₂ (837.90): C, 45.87; H, 2.41; Cu, 7.58; N, 10.03; Found: C, 45.65; H, 2.33; Cu, 7.63; N, 9.97%; UV-Vis (DMF)(λ_{max} /nm): 404.

2,2'-{Benzene-*o*-diylbis[nitrilomethylidene]}bis(4-((*p*-trifluoromethoxy)phenyl)diazanyl)phenoxy) copper complex (*CuL*³): Yield: 73%; IR (KBr, cm⁻¹): 1604 (C=N), 1380 (C-O), 537 (Cu-O), 439 (Cu-N); Anal. Calcd. for C₃₄H₂₀CuF₆N₆O₄: C, 71.27; H 4.58; N, 8.31. Found: C, 71.43, H, 4.54, N, 8.52%; UV-Vis (DMF) (λ_{max} /nm): 408.

2,2'-{Benzene-*o*-diylbis[nitrilomethylidene]}bis(4-((*o*-ethoxyphenyl)diazanyl)phenoxy) copper complex (*CuL*⁴): Yield: 82%; IR (KBr, cm⁻¹): 1607 (C=N), 1397 (C-O), 542 (Cu-O), 437 (Cu-N); Anal. Calcd. for C₃₆H₃₀CuN₆O₄: C, 64.13; H, 4.49; N, 12.47. Found: C, 64.34, H, 4.61, N, 12.31%; UV-Vis (DMF) (λ_{max} /nm): 406.

2,2'-{Benzene-*o*-diylbis[nitrilomethylidene]}bis(4-((3,5-dimethoxyphenyl)diazanyl)phenoxy) copper complex (*CuL*⁵): Yield: 78%; IR (KBr, cm⁻¹): 1599 (C=N), 1430 (C-O), 523 (Cu-O), 419 (Cu-N); Anal. Calcd. for C₃₆H₃₀CuN₆O₆: C, 61.23; H, 4.28; Cu, 9.00; N, 11.90. Found: C, 61.11, H, 4.14, Cu, 8.79; N, 11.74%; UV-Vis (DMF) (λ_{max} /nm): 400.

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