

## Synthesis and characterization of mono- and bimetallic complexes of Zn(II) and Cu(II); new multifunctional unsymmetrical acyclic and macrocyclic phenol-based ligand

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### ABSTRACT

The dicompartmental macrocyclic ligand ( $L^{2-}$ )<sup>2-</sup> was prepared by [1:1] cyclic condensation of *N,N'*-dimethylacetate-*N,N'*-ethylene-di(5-methyl-3-formyl-2-hydroxybenzylamine) with 1,3-diaminopropane. The ligand includes dissimilar N(amine)<sub>2</sub>O<sub>2</sub> and N(imine)<sub>2</sub>O<sub>2</sub> coordination sites sharing two phenolic oxygen atoms and containing two methyl acetate pendant arms on the amine nitrogen donor atoms. A series of mono- and bimetallic complexes were synthesized and characterized on the basis of elemental analysis, molar conductance measurement, IR and UV-Vis spectroscopy techniques. It was found that during the cyclization process the copper (II) displaced from the N(amine)<sub>2</sub>O<sub>2</sub> to the N(imine)<sub>2</sub>O<sub>2</sub> coordination site and one of the methyl acetate pendant arms is dissociated. The heterodinuclear complex of  $[ZnL^2Cu(\mu-OAc)]^+$  was prepared by a transmetallation reaction on the  $[ZnL^2Zn(\mu-OAc)]^+$  by Cu(II). The characterization results showed that the two metal ions are bridged by two phenolic oxygen atoms and an acetate group, providing distorted five-coordination geometries for the both metal ions.

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## 1. Introduction

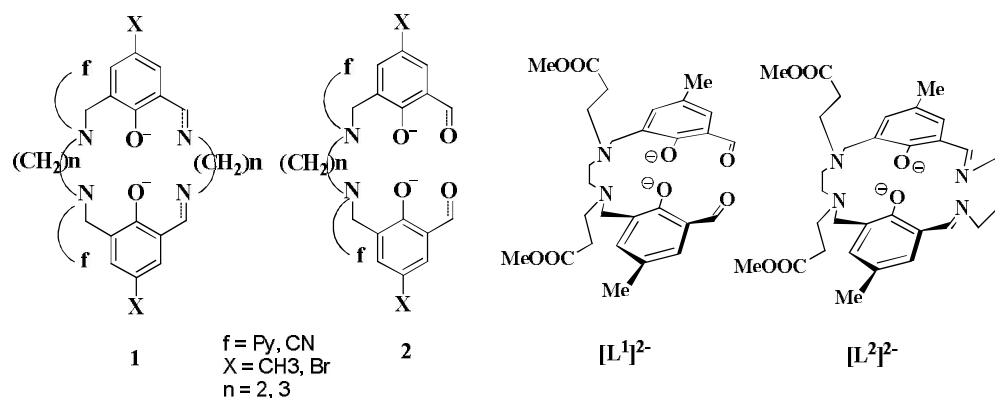
In the last decade, great attention was paid to the design and synthesis of dicompartmental ligands capable of forming macrocyclic or acyclic complexes with similar or dissimilar metal ions<sup>1</sup>. Interest in this topic is due partly to their potential applications to mimic bimetallic biosides of the metalloenzymes<sup>1</sup> and their interesting catalytic properties<sup>2</sup>. Among many different types of dicompartmental ligands, phenol-based ligands having two metal binding sites sharing two phenolic oxygen atoms have been proved as more relevant for modeling of the active sites of many

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metallobiosites to hosting and carrying small molecules<sup>3</sup>. Therefore, synthesis of such compartmental ligands and their metal complexes are desirable. Zinc(II) complexes, which are thermally stable, structurally diverse and easily modified, have been attracted great attention due to their biomimicking roles. Furthermore, some synthetic dinuclear zinc(II) complexes are also known to participate in some bio-related processes<sup>4</sup>. Copper (II) complexes are the beacon for modeling, and they serve as bioinorganic model compounds not only in enzymatic reactions, but also in catalytic synthetic oxidation reactions<sup>5</sup>.

In our previous work we have succeeded in preparing a family of macrocyclic phenol-based ligands of the type **1**, and acyclic dicompartmental type **2**, which are shown in Scheme 1 in our laboratory and their structures and reactivities were investigated<sup>6-12</sup>. In present study, we have reported the synthesis of a new multifunctional phenol-based ligand,  $L^1H_2$  (Scheme 1), with the new methyl propionate arms, which has potentially a tetra-coordinate compartment with an  $O_4$  donor set, comprising of two phenolic and two formyl oxygen atoms and another a hexa-coordinate compartment with an  $N_2O_4$  donor set, made by oxygen atoms of two phenolic, two carboxylate groups and two aminic nitrogen atoms. The acyclic monometallic complexes  $[ML^1]$  was cyclized by 1,3-diaminopropane to produce dicompartmental macrocyclic ligand  $[L^2]^{2-}$  shown in Scheme 1.

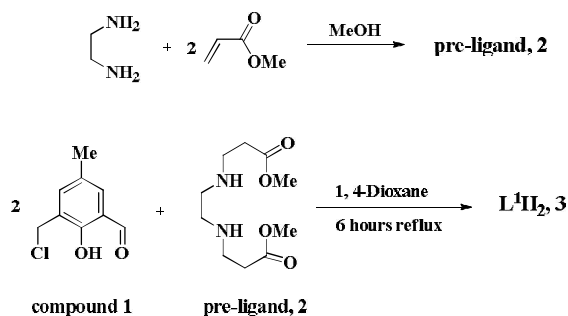


Scheme 1. Dicompartmental ligands

## 2. Results and Discussion

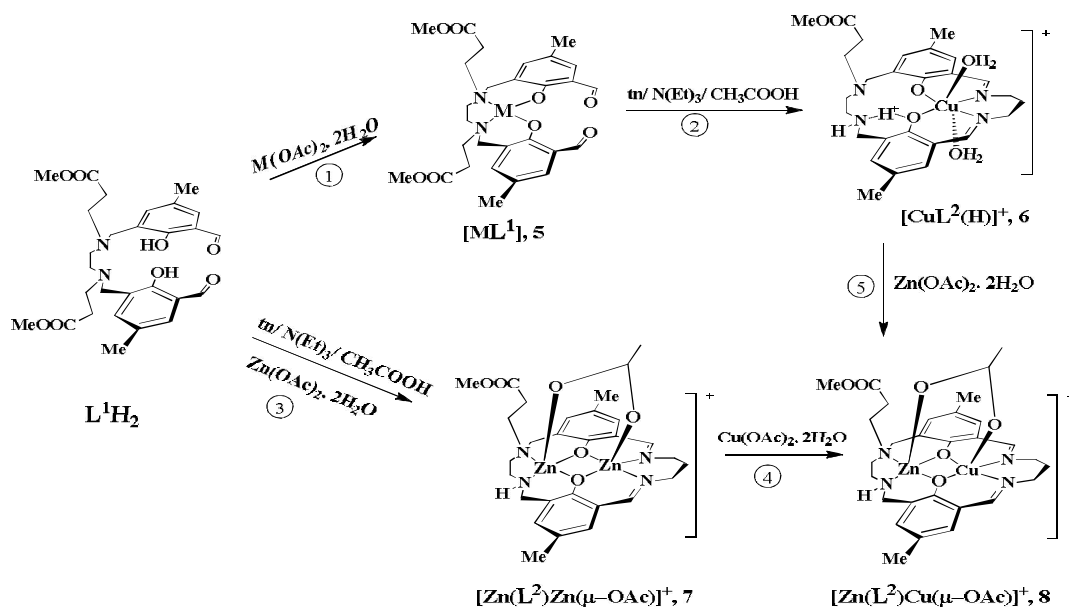
### 2.1. Syntheses

The acyclic ligand  $L^1H_2$ , **3**, was prepared by the sequence of reactions outlined in Scheme 2. The pre-ligand **2** was synthesized first by reaction of ethylenediamine and acryl amide with mole ratio of 1:2, respectively in solvent of methanol. In the next step, condensation of one part of compound **1** and two parts pre-ligand **2** afforded ligand  $L^1H_2$ , **3**. The IR spectra of  $L^1H_2$ , showed a broad band at around  $3423 \text{ cm}^{-1}$ , which is probably attributed to the OH stretching vibration of the phenolic groups. The mononuclear  $[Zn^{II}L^1]$  and  $[Cu^{II}L^1]$  complexes were readily prepared as solid by reaction of  $L^1H_2$  with the metal acetate and triethylamine in ethanol (Scheme 2, reaction 1).



Scheme 2. General method for the preparation of pre-ligand and  $L^1H_2$

The metal ion in the acyclic  $[M^{\text{II}}L^1]$  complex can bind at either the  $N(\text{amine})_2O_2$  or at the  $O_4$  coordination site of the ligand. The IR spectra and the visible spectral data as will be discussed later show that the metal ion positioned in the  $N(\text{amine})_2O_2$  coordination site. However, through characterization and establishment of the purity of these compounds were hindered by their poor solubility in all of the solvent investigated. In the next step, the monometallic acyclic complex  $[M^{\text{II}}L^1]$  was cyclized by addition of 1,3-diaminopropane under acid catalysis as shown in Scheme 2 (reaction 2). The elemental analysis of the copper (II) complex reveals that one of the pendent arm is removed and the Cu(II) ion coordinated into  $O_2N_2(\text{imine})$  site and the other aminic site,  $O_2N_2(\text{amine})$  is occupied by a proton. Although the exact nature of this phenomenon is not known, the arm rupture and copper displacement was observed before<sup>8</sup>. However, the formulation  $[(H^+)L^2Cu]PF_6$  and a structure such as that shown in Scheme 3 would be consistence with the characterization results. All attempts to prepare monometallic macrocyclic complex Zn(II) by cyclization of  $[ZnL^1]$  and 1,3-diaminopropane with alteration of reaction conditions were failed and resulted in the formation of bimetallic complex  $[Zn(L^2)Zn(\mu-OAc)]PF_6$ , **7**, as depicted in Scheme 3 (reaction 3).



**Scheme 3.** The synthesis steps for preparation of bimetallic complexes

It seems this phenomenon depends on the nature of the  $M(\text{II})$  ion used. However, the analogous ligand system with two pyridine pendant arms instead of the methylpropionate produced the macrocyclic mononuclear complex as  $[ZnL^2(H^+)_2]^{2+}$ <sup>13</sup>. The removal of a methyl propionate pendant arm in reaction 1 in Scheme 3 that is, the introduction of  $Cu(OAc)_2$  to the free ligand  $L^1H_2$ , was excluded due to the lack of the N-H vibration signal in the IR spectrum of  $[CuL^1]$  complex and also by similarity of its IR spectrum with that of the  $[ZnL^1]$  complex. The driving force in the displacement of the Cu(II) ion may be in part, which is related to the nature of the donor atoms of two coordination site. The Cu(II) migrates to occupy the relatively rigid  $N(\text{imine})_2O_2$  coordination site, which provides the more preferred square coplanar environment but Zn(II) exists in the more flexible  $N(\text{amine})_2O_2$  site<sup>14</sup>.

The heterobimetallic complex including a copper (II) ion in the  $N(\text{imine})_2O_2$  and zinc (II) ion in the  $N(\text{amine})_2O_2$  compartments were synthesized by two different routes. The monometallic  $[(H^+)L^2Cu]^+$  complex offers a perfect precursor for the mild preparation of the heterobimetallic complex of  $[ZnL^2Cu(\mu-OAc)]^+$ . The reaction 5 depicted in Scheme 3 can be driven to the right by addition of a base and are exceptionally mild since incorporation of the second metal depends on the fast removal of the cavity proton. Under such conditions it would be anticipated that the coordination

of the second metal ion would be much faster than the site scrambling of the metal<sup>15</sup>. The heterobimetallic complexes  $[\text{ZnL}^2\text{Cu}(\mu\text{-OAc})]\text{PF}_6$  were prepared by reaction of monometallic  $[(\text{H}^+)\text{L}^2\text{Cu}]^+$  complex with  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  as illustrated in Scheme 3 (reaction 5). Alternatively, the heterobimetallic  $[\text{ZnL}^2\text{Cu}(\mu\text{-OAc})]\text{PF}_6$  complex was prepared through a transmetallation reaction via the second route (reaction 4 in Scheme 3). The reaction was simply carried out by addition of  $\text{Cu}(\text{OAc})_2$  to the homobimetallic  $[\text{ZnL}^2\text{Zn}(\text{OAc})]^+$  complex at room temperature with a moderate yield. It was found that the optimum mole ratio of the reactants between  $[\text{ZnL}^2\text{Zn}(\mu\text{-OAc})]^+$  and  $\text{Cu}(\text{OAc})$  is 1:1.2.

### Physical Characterization

The IR spectra of ligand  $\text{L}^1\text{H}_2$  and all complexes show a band at  $1729\text{ cm}^{-1}$  associated to the presence of the carbonyl group of the pendent arm(s) and it remains unchanged in all the complexes, indicating that the carbonyl group(s) is free of coordination in complexes. The vibration band around  $1680\text{ cm}^{-1}$  is due to the presence of  $\nu(\text{C}=\text{O})$  aldehyde groups in the ligand  $\text{L}^1\text{H}_2$ . This band appears at  $1606\text{ cm}^{-1}$  for the mononuclear copper complexes,  $[\text{ML}^1]$ . This displacement to the lower wave numbers is due to coordination of the  $\text{M}(\text{II})$  ion into the  $\text{N}_2\text{O}_2$  coordination site. Appearance of a band at near  $1550\text{ cm}^{-1}$  for all of the complexes is assigned to be the skeletal vibration of the aromatic rings<sup>16</sup>. Further, the appearance of new bands at  $845$  and  $559\text{ cm}^{-1}$  in  $[(\text{H}^+)\text{L}^2\text{Cu}]\text{PF}_6$  and in the bimetallic complexes correspond to the vibration modes of  $\text{PF}_6^-$  ion<sup>17</sup>. Also the cyclization was confirmed by the disappearance of the aldehyde  $\text{C}=\text{O}$  stretching band at around  $1606\text{ cm}^{-1}$  and the emergence of a strong band at around  $1629\text{ cm}^{-1}$  that is assigned to  $\text{C}=\text{N}$  stretching vibration mode<sup>18,19</sup>. The N-H vibration of the quaternized amine appears at near  $3240\text{ cm}^{-1}$  in the complexes  $[(\text{H}^+)\text{L}^2\text{Cu}]\text{PF}_6$ ,  $[\text{ZnL}^2\text{Zn}(\mu\text{-OAc})]\text{PF}_6$  and  $[\text{ZnL}^2\text{Cu}(\mu\text{-OAc})]\text{PF}_6$  indicate the breakage of an methyl propionate pendant arm and meanwhile the presence of the  $\nu(\text{C}=\text{O})$  vibration at  $1730\text{ cm}^{-1}$  point out existence of a propionate pendant pendent arm. These results reveal that the only one of the pendent arms is removed. A strong evidence for the coordination of the second metal in the  $\text{N}(\text{imine})_2\text{O}_2$  or  $\text{N}(\text{amine})_2\text{O}_2$  coordination site is the appearance of the phenolic stretching band at  $1320\text{-}1334\text{ cm}^{-1}$ , which is absent in this region in the monometallic complexes<sup>19</sup>. The IR spectra of the bimetallic complexes show the symmetric and anti-symmetric  $\nu(\text{COO})$  vibration bands of the acetate group at around  $1572$  and  $1462\text{ cm}^{-1}$ , respectively. The small separation between the two vibration bands (less than  $150\text{ cm}^{-1}$ ) is in agreement with the bridging function of the acetate group in the complex<sup>20</sup>.

**Table 1.** Electronic absorption maxima (nm) and intensities ( $\text{M}^{-1}\text{ cm}^{-1}$ ) of the charge transfer and d-d transitions for  $\text{Cu}(\text{II})$  complexes in  $\text{CH}_3\text{CN}$

Compound	$\pi - \pi^*$	d-d
$[\text{CuL}^1]$	415 (3720) <sup>a</sup>	689 (127) <sup>a</sup>
$[\text{ZnL}^1]$	380 (3830) <sup>a</sup>	-
$[(\text{H}^+)\text{L}^2\text{Cu}]\text{PF}_6$	375 (2790)	- <sup>b</sup>
$[\text{ZnL}^2\text{Zn}(\mu\text{-OAc})]\text{PF}_6$	391 (3450)	-
$[\text{ZnL}^2\text{Cu}(\mu\text{-OAc})]\text{PF}_6$	398 (3100)	590 (72)

<sup>a</sup> taken in solvent of DMSO

<sup>b</sup> d-d transition was not observed due to tailing of charge transfer band

The electronic absorption spectra of the mono- and bimetallic complexes were run in acetonitrile solutions over the range 200–900 nm. The spectra of the complexes are dominated by charge transfer band and other ligand-based transitions. Azomethine  $\pi \rightarrow \pi^*$  transitions appear at around 280 nm for monometallic complexes consistent with the other monometallic related complexes reported<sup>21</sup>. These bands typically shift to about 350–360 nm in the bimetallic complexes. In the copper complexes the charge transfer bands overlap with the d-d band. The bands at 689 nm in  $[\text{CuL}^1]$  and 590 nm in  $[\text{ZnL}^2\text{Cu}(\mu\text{-OAc})]\text{PF}_6$  complexes are clearly due to the d–d transition of the copper(II) center<sup>14</sup>. The variation in the position of the d-d band undoubtedly reflects a difference in the coordination geometry and perhaps coordination number of the  $\text{Cu}(\text{II})$  ion in the respective coordination site. The d-d band of  $[\text{CuL}^1]$  complex is also compared to those of related copper(II) complexes with

propionitrile pendent arm that have similar structures (665 nm)<sup>8</sup>. These results supports that the copper(II) ion displaced from N(amine)<sub>2</sub>O<sub>2</sub> coordination site to the N(imine)<sub>2</sub>O<sub>2</sub> coordination site upon the cyclization of [CuL<sup>1</sup>] and the N(amine)<sub>2</sub>O<sub>2</sub> coordination site is free from coordination or occupied by zinc(II) ion (see Scheme 2). In [(H<sup>+</sup>)L<sup>2</sup>Cu]<sup>+</sup> the charge transfer band appears as a lower energy shoulder on the more intense azomethine transition, which may entirely obscure the d-d band.

Molar Conductivity measurement of the [CuL<sup>1</sup>] and [ZnL<sup>1</sup>] complexes showed lack of conductivity in DMSO solution. Molar conductance of all the ionic complexes fall within the range reported for 1:1 electrolytes (123–155 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>) in acetonitrile solutions at 25°C<sup>20</sup>. A two-ion electrolyte observed in the mononuclear macrocyclic complex [(H<sup>+</sup>)L<sup>2</sup>Cu]PF<sub>6</sub>, confirms the presence of one proton in the N<sub>2</sub>O<sub>4</sub> coordination site.

### 3. Conclusions

The aim of the present study involves the synthesis of novel unsymmetrical mono- and homo/heterobimetallic Cu(II) and Zn(II) complexes utilizing new dicompartmental acyclic and macrocyclic ligands possessing two contiguous hexa- and tetra-coordination sites. Although, the synthetic objective of this research has been achieved, the characterization results showed that the propionate pendant pendent arms are free from coordination. An interesting result observed when acyclic monometallic copper (II) complex was cyclized by 1,3-diaminopropan, which the copper ion was displacement from N(amine)<sub>2</sub>O<sub>2</sub> to the N(imine)<sub>2</sub>O<sub>2</sub> coordination sites along with dissociation of an pendent arm. To achieve our primarily objective that is the preparation of dicompartmental ligands possessing contiguous six- and four-coordination sites the ligand system requires to be modified in order to bring the pedant arms in coordination to the metal ion. In view of the present results, the ester moieties of the pedant arms are not able to coordinate to the metal ions but it seems probable to hydrolyze the –COOMe to –COO<sup>-</sup> group which contain better donor set atoms. This transformation is currently in progress in our lab.

### Acknowledgements

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### 4. Experimental

#### 4.1. Materials and Methods

C, H, N analyses of the complexes were carried out using LECO CHN-600 elemental analyzer (Germany). IR spectra were recorded on a Perkin-Elmer FTIR spectrophotometer (Germany) on KBr disks in the range 400–4000 cm<sup>-1</sup>. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker 400 DRX Fourier Transform Spectrometer (Germany). Molar conductivity was measured at room temperature by using a JENWAY digital conductivity meter (Spain), using freshly prepared solutions of the complexes in 0.005 M acetonitrile or dimethyl sulfoxide solvent. Electronic spectra of the complexes were performed on an UV-2100 (China) spectrophotometer in CH<sub>3</sub>CN and DMSO solutions. All samples were dried to constant weights under vacuum. All solvents and chemicals were of analytical grade and used without further purification, except for ethylenediamine that was purified by a general method. The precursor compound, 3-(chloromethyl)-2-hydroxy-5-methylbenzaldehyde, **1**, was prepared according to published procedures<sup>22,23</sup>. The method for preparation another precursor compound, *N,N*-bis(2-acrylomethyl)-ethylenediamine, **2**, has been described through this paper.

#### 4.2. General procedure

**Synthesis of pre-ligand *N,N*-bis(2-acrylomethyl)-ethylenediamine, 2:** Methyl acrylate (2.3 mL 0.04 mmol) was added drop-wise to a solution of ethylenediamine (1.3 mL, 0.02 mmol) in methanol

(25 mL) during 45 min. Temperature should be controlled and gradually increased to 40°C through the progress of the reaction (higher temperature can cause a tar like by-product). Then the solvent was removed under reduced pressure. Furthermore, the residual of the water was removed by passing the product through anhydrous CaCl<sub>2</sub>. The obtained product was as a pale yellow liquid. Yield: 99%. Selected IR data (v/cm<sup>-1</sup>): 3289 (m, N-H str.), 2949 (m, C-H str. aliphatic), 1732 (s, C=O str.), 1219 (s, C-N str.). <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O), δ (ppm): 2.49 (t, 4H, *J*=7.2 Hz, -CH<sub>2</sub>CH<sub>2</sub>COOMe), 2.52 (s, 2H, -NCH<sub>2</sub>CH<sub>2</sub>N-), 2.72 (t, 4H, *J*=7.2 Hz, -CH<sub>2</sub>CH<sub>2</sub>COOMe), 3.60 (s, 6H, -COOCH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O), δ (ppm): 30.97 (-CH<sub>2</sub>CH<sub>2</sub>COOMe), 48.42 (-CH<sub>2</sub>CH<sub>2</sub>COOMe), 50.01 (-NCH<sub>2</sub>CH<sub>2</sub>N-), 52.19(-COOCH<sub>3</sub>), 175.35 (-COOMe).

**Synthesis of the dicompartmental ligand. L<sup>1</sup>H<sub>2</sub>, 3:** To a solution of 3-(chloromethyl)-2-hydroxy-5-methylbenzaldehyde(I) (0.92 g, 5 mmol) in 1,4-dioxane (25 mL) was added anhydrous K<sub>2</sub>CO<sub>3</sub> (1.38 g, 2.7 mmol). The yellow mixture was treated with the dropwise addition of a solution of *N,N*-bis(2-acrylomethyl)-ethylenediamine (0.42 g, 2.5 mmol) in ethanol (5 mL). The resultant mixture was refluxed for 6 h. After removing K<sub>2</sub>CO<sub>3</sub> by filtration through celite, the solvent was removed under reduced pressure. The resultant crude product was purified by method found in the literature<sup>24</sup> to obtain a brown oily product. Yield: 20%. Selected IR data (v/cm<sup>-1</sup>): 3417 (br., O-H), 2949 (s, C-H str. aliphatic), 1411 (s, C=C aromatic), 1219 (s, C-O str.). <sup>1</sup>H NMR (400 MHz in CDCl<sub>3</sub>) δ (ppm): 2.37 (s, 6H, -CH<sub>3</sub>), 2.43 (s, 2H, -NCH<sub>2</sub>CH<sub>2</sub>N-), 2.60 (t, *J*=7.2 Hz, 4H, -CH<sub>2</sub>CH<sub>2</sub>COOMe), 3.68 (s, 6H, -COOCH<sub>3</sub>), 3.78 (t, *J*=7.2 Hz, 4H, -N-CH<sub>2</sub>-CH<sub>2</sub>-COOMe), 4.68 (s, 2H, Ar -CH<sub>2</sub>-N), 7.32 (s, 1H, Ar), 7.47 (s, 1H, Ar), 9.87 (s, 1H, -CH=O), 11.27 (s, 1H, Ar-OH).

**Synthesis of monometallic complex [ZnL<sup>1</sup>], 4:** To the free ligand L<sup>1</sup>H<sub>2</sub> (0.1g, 0.2 mmol) in methanol (5 mL), was added Et<sub>3</sub>N (0.007 mL, 0.5 mmol). The brown mixture was stirred for 1h and Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.006 g, 0.25 mmol) was then added which a yellow solid formed. The resulting product was collected, washed with ethanol (2×5 mL), Et<sub>2</sub>O (2×5 mL) and n-hexane (2×5 mL) and was dried under vacuum. Yield: 25%. Selected IR data (v/cm<sup>-1</sup>): 3423 (b, OH), 2923 (m, C-H str. aliphatic), 1731 (s, C=O str.), 1637 (s, HC=O str.), 1464 (s, C=C aromatic), 1226 (s, C-O str.). Λ<sub>m</sub> = 16.8 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> in DMSO.

**Synthesis of monometallic complex [Cu(L<sup>1</sup>)], 5:** The copper complex was prepared by the same procedure as above which resulted in a green solid. Yield: 17%. UV-Vis [λ<sub>max</sub> in nm (ε in L mol<sup>-1</sup> cm<sup>-1</sup>) in DMSO]: 415 (3219), 690 (127). Selected IR data (v/cm<sup>-1</sup>): 3417 (br, OH), 2921 (m, C-H str. aliphatic), 1727 (s, C=O str.), 1606 (s, HC=O str.), 1466 (s, C=C aromatic), 1226 (s, C-O str.). Λ<sub>m</sub> = 21.2 Ω<sup>-1</sup> mol<sup>-1</sup> cm<sup>2</sup> in DMSO.

**Synthesis of monometallic complex [(H<sup>+</sup>)L<sup>2</sup>Cu]PF<sub>6</sub>·H<sub>2</sub>O, 6:** To the stirred suspension of the precursor complex, 2 (0.527 g, 1 mmol) in methanol (20 mL), was added dropwise over 1 h a solution of 1,3-diamino propane (0.009 mL, 1.05 mmol) in the presence of acetic acid (0.012 mL, 2.09 mmol) in absolute ethanol (10 mL). After the addition was completed, all the starting materials were dissolved. The green solution was then stirred for 1 h at ambient temperature. A green solid precipitated almost immediately after the addition of a filtered solution of NH<sub>4</sub>PF<sub>6</sub> (0.23 g, 2.5 mmol) in ethanol (10 mL). The solid was collected and washed with ethanol (2×10 mL), Et<sub>2</sub>O (2×5 mL) and n-hexane (2×5 mL). The crude compound was recrystallized by diffusion of ethanol into CH<sub>3</sub>CN solution, which, yielded in green solid. Yield: 57%. Anal. calc. for C<sub>27</sub>H<sub>39</sub>N<sub>4</sub>O<sub>6</sub>F<sub>6</sub>PCu (Mw = 724.13 g mol<sup>-1</sup>) (%): C, 44.78; H, 5.43; N, 7.74; found: C, 44.93; H, 5.52; N, 8.26. UV-Vis [λ<sub>max</sub> in nm (ε in L mol<sup>-1</sup> cm<sup>-1</sup>) in CH<sub>3</sub>CN]: 375 (2791). Selected IR data (v/cm<sup>-1</sup>): 3414 (br, OH), 2923 (m, C-H str. aliphatic), 1729 (s, C=O str.), 1629 (s, C=N str.), 1458 (s, C=C aromatic), 844, 560 (s, PF<sub>6</sub><sup>-</sup>). Λ<sub>m</sub> = 155 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> in CH<sub>3</sub>CN.

**Synthesis of bimetallic complex [Zn(L<sup>2</sup>)Zn(μ-OAc)]PF<sub>6</sub>·CH<sub>3</sub>CN, 7:** To the free ligand L<sup>1</sup>H<sub>2</sub> (0.527 g, 1 mmol) in methanol (20 mL), was added Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.5 g, 2.5 mmol). After stirring

for 1 h a solution of 1,3-diaminopropane (0.009 mL, 1.05 mmol) in the presence of acetic acid (0.012 mL, 2.09 mmol) in absolute ethanol (10 mL) was then added during 1 h while stirring. Upon addition of a filtered solution of  $\text{NH}_4\text{PF}_6$  (0.23 g, 2.5 mmol) in methanol (20 mL) to the resulting clear brown solution a yellow solid precipitated almost immediately. The solid was collected, washed with ethanol ( $2 \times 5$  mL),  $\text{Et}_2\text{O}$  ( $2 \times 5$  mL) and n-hexane ( $2 \times 5$  mL) and dried at ambient temperature. It was recrystallized from diffusion of diethyl ether into acetonitrile solution. Yield: 57 %. Anal. calc. for  $\text{C}_{31}\text{H}_{41}\text{F}_6\text{N}_5\text{O}_6\text{PZn}_2$  (MW = 854.40  $\text{g mol}^{-1}$ ) (%): C, 43.58; H, 4.72; N, 8.20; found: C, 43.10; H, 5.22; N, 8.52. UV-Vis [ $\lambda_{\text{max}}$  in nm ( $\epsilon$  in  $\text{L mol}^{-1} \text{cm}^{-1}$ ) in  $\text{CH}_3\text{CN}$ ]: 391 (3451). Selected IR data ( $\nu/\text{cm}^{-1}$ ): 3423 (br., OH), 2924 (m, C-H str. aliphatic), 1729 (s, C=O str.), 1629 (s, C=N str.), 1460 (s, C=C aromatic), 845, 559 (s,  $\text{PF}_6^-$ ).  $\Lambda_m = 135 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  in  $\text{CH}_3\text{CN}$ .

**Synthesis of monometallic complex  $[\text{Zn}(\text{L}^2)\text{Cu}(\mu\text{-OAc})]\text{PF}_6 \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{CN}$ , 8;** Route 1: To a solution of complex 7 (0.42 g, 0.05 mmol) in  $\text{CH}_3\text{CN}$  (5 mL) was added a solution of  $\text{Cu}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (0.2 g, 0.05 mmol) in ethanol. The green mixture was stirred for 3 h. The solution was partially concentrated at room temperature to reduce the  $\text{CH}_3\text{CN}$  content. Also ethanol was added (3 mL) and the solution was allowed to stand overnight. The dark green solid was collected and washed successively with MeOH ( $2 \times 10$  mL),  $\text{Et}_2\text{O}$  ( $2 \times 5$  mL) and n-hexane ( $2 \times 5$  mL), then dried under vacuum. Yield: 60%. Anal. Calc. for  $\text{C}_{31}\text{H}_{42}\text{CuF}_6\text{N}_5\text{O}_7\text{PZn}$  (MW = 870.58  $\text{g mol}^{-1}$ ) (%): C, 42.77; H, 4.86; N, 8.04; found: C, 42.37; H, 5.09; N, 8.06. UV-Vis [ $\lambda_{\text{max}}$  in nm ( $\epsilon$  in  $\text{L mol}^{-1} \text{cm}^{-1}$ ) in  $\text{CH}_3\text{CN}$ ]: 398 (3106), 590 (72). Selected IR data ( $\nu/\text{cm}^{-1}$ ): 3420 (br, OH), 2923 (m, C-H str. aliphatic), 1728 (s, C=O str.), 1628 (s, C=N str.), 1456 (s, C=C aromatic), 845, 559 (s,  $\text{PF}_6^-$ ).  $\Lambda_m = 123 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  in  $\text{CH}_3\text{CN}$ .

Route 2: To a solution of complex 7 (0.42 g, 0.05 mmol) in  $\text{CH}_3\text{CN}$  (5 mL) was added a solution of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (0.1 g, 0.05 mmol) in ethanol. The green mixture was stirred for 1 h. The solution was partially concentrated at room temperature to reduce the  $\text{CH}_3\text{CN}$  content. The dark green solid was collected and washed successively with MeOH ( $2 \times 10$  mL),  $\text{Et}_2\text{O}$  ( $2 \times 5$  mL) and n-hexane ( $2 \times 5$  mL), then dried under vacuum. Yield: 66%.

The identity of the compound obtained was confirmed by elemental analysis, IR, UV-Vis spectra and molar conductance value, whose characteristics compared well with that prepared by route 1.

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