Synthesis and characterization of mono- and heterodinuclear complexes of dinucleating macrocyclic ligand bearing hexa- and pentadentate coordination sites

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Abstract: Macrocyclic heterobinuclear Zn(II)–Cu(II) complexes with phenol based dicompartmental ligands possessing contiguous hexa- and penta-coordination sites were prepared by a stepwise procedure. The ligands include similar N_4O_2 and dissimilar $N(imine)_3O_2$ and $N(amine)_3O_2$ coordination sites sharing two phenolic oxygen atoms. The six-coordination site comprises two pyridyl pendant arms on the amine nitrogen atoms, while the five-coordination site consists of dipropylenetriamine moieties. The prepared mono- and dinuclear complexes were characterized by elemental analysis, molar conductance measurements, IR, NMR and UV-Vis spectroscopy techniques. Characterization results confirm that in the mononuclear macrocyclic zinc complexes two pyridyl moieties located in the expected *trans* positions and two protons occupied the N_3O_2 coordination site. In contrast, the dinuclear macrocyclic Zn(II)-Cu(II) complexes the Zn(II) ions located in six coordination site with *cis* disposed pyridyl ligands and the penta-dantate compartment is occupied by Cu(II) ion in a square pyramidal geometry. The origins of the structural variations are discussed.

Key words: Dicompartmental ligand; Heterodinuclear complex; Macrocyclic; Phenol-based ligand; dipropylenetriamine link

1. Introduction

In the recent years, great attention was paid to the design and synthesis of dicompartmental ligands capable of forming macrocyclic complexes with similar or dissimilar metal ions [1]. Interest in this area is due partly to their potential applications in catalytic properties [2], ability to stabilize unusual oxidation states [3] and importance in biomimetic studies of dinuclear metalloproteins [4]. 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 the active sites of many metallobiosites [5-11] to hosting and carrying small molecules [12]. As a result, synthesis of such compartmental ligands and their metal complexes are desirable in view of chemists. The compartmental ligands could be symmetrical or unsymmetrical in which special focus was on the unsymmetrical phenol base compounds. The unsymmetrical could be with respect to the cavity size, coordination number, geometric requirement, or the nature of the donor atoms [13]. Okawa investigated the compartmental ligands with inactive pendant arms that provide two unsymmetrical tetra-coordination sites [14,15]. Research conducted by Bosnich [16,17], Busch [18], and us [19,20] shown that by suitable design of the ligands with active pendant arms, dicompartmental

ligand with hexa- and tetra coordinated sites can be achieved. These ligands potentially can provide dinuclear complexes with one coordinatively saturated and another unsaturated metal. Some types of mono and dinuclear complexes of macro –cyclic ligands (A in Scheme 1) have been prepared and their structures and reactivities were investigated in our laboratory [21-24]. In present study, we have reported the synthesis of new multifunctional phenol-based ligands, LH_2 (Scheme 1), with dipropylenetriamine link, which has potentially a penta-coordinate compartment with an N_3O_2 donor set, comprising of two phenolic and three nitrogen atoms (=N-$(CH_2)_3$-NH-$(CH_2)_3$-N= or -HN-$(CH_2)_3$-NH-$(CH_2)_3$-NH-) and another a hexa-coordinate compartment with an N_4O_2 donor set, made by oxygen atoms of two phenolic, two pyridyl groups and two aminic nitrogen atoms.
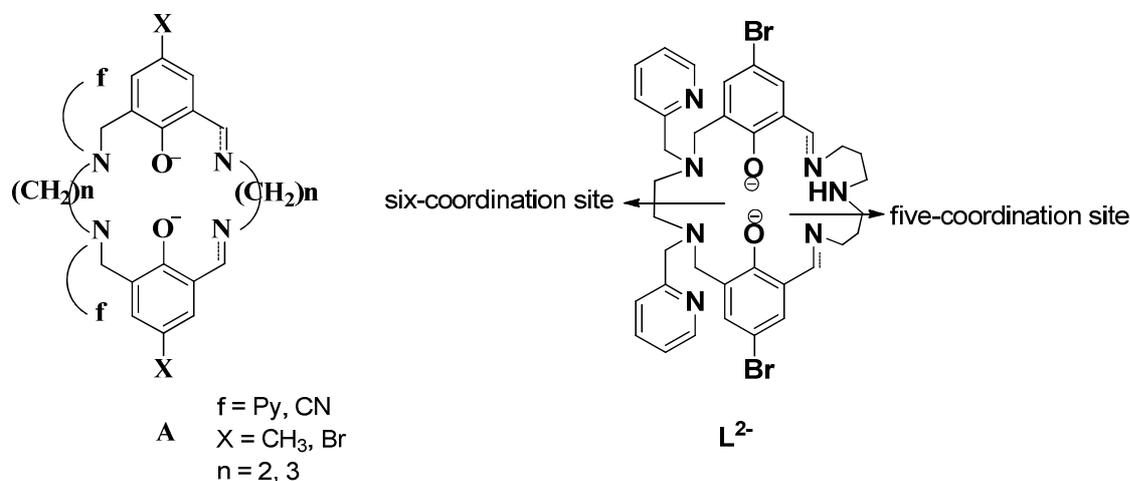
Scheme 1: Dicompartmental ligands.

2. Experimental

2.1. Materials and methods

All of the chemicals and solvents were purchased from Aldrich and Merck. The ligand L^1H_2, **3** was synthesized as previously described [17] and the

dialdehyde complex, **4**, [Zn(II)L^1] was prepared according to the literature method [18,19]. All the samples were dried to constant weight under high vacuum prior to analysis. ^{1}H NMR spectra were obtained on a Bruker 400MHz DRX spectrometer in

solvent of CD_3CN. IR spectra were recorded as pressed KBr discs, using a Bruker FT-IR instrument. Electronic spectral measurements were carried out using a Baric2100 model UV-Vis spectrophotometer in the range of 200-900 nm. C, H, N elemental analysis was performed on a LECO 600 CHN elemental analyzer. Conductivity measurements were carried out at 25^oC with a Jenway 400 conductance meter using 10^{-3} M solution of the complexes in solvent of CH_3CN.

Caution: Perchlorate salts are potentially explosive and should be handled with appropriate care.

2.2. Synthesis of complexes

$[Zn^{II}L^2(H^+)_2](ClO_4)_2 \cdot H_2O$, 5: to the stirred suspension of compound 4 (0.5 g, 0.68 mmol) in ethanol (30 mL) was added dropwise over 1h a solution of dipropylenetriamine (0.095 mL, 68 mmol) and acetic acid (0.077 mL, 1.36 mmol) in ethanol (20 mL). After the addition was completed, all the starting materials were dissolved. The yellow solution was then stirred for 3 h at room temperature. A yellow-orange solid precipitated almost immediately after the addition of a filtered solution of NH_4ClO_4 (1.0 g, 10 mmol) in ethanol (12 mL). The solid was collected and was washed with ethanol (2 × 10 mL), Et_2O (2 × 10 mL) and n-hexane (2 × 10 mL). The crude solid was recrystallized from CH_3CN / EtOH as follow: the crude compound was dissolved in CH_3CN (ca. 4 mL) at room temperature and the solution was filtered. To the CH_3CN solution was added absolute ethanol (ca. 4 mL) and the resulting solution was placed in a small flask, which was then put in a bigger jar containing ethanol (ca. 25 mL). This jar was capped to allow for slow diffusion of ethanol in the solution. After several days the complex was collected and dried under vacuum

which, yielded yellow-orange crystals, (0.46 g, 65%). Anal. calcd. for $C_{36}H_{41}N_7O_{10}Cl_2ZnBr_2 \cdot H_2O$ (M_w = 1045.68 g. mol^{-1}) (%): C, 41.34; H, 4.14; N, 9.37. Found: C, 41.35; H, 3.86; N, 8.84. FT-IR (KBr, cm^{-1}): 3436 (b, N-H), 2925 (m, C-H), 1651 (s, C=N), 1436 (s, Ph-O), 1094 (s, ClO_4), 623 (m, ClO_4). ^1H NMR (400 MHz, CD_3CN), δ (ppm): 1.98-2.00 (m, 3H), 2.80-3.10 (m, AB system, 5H), 3.28-3.56 (m, 1H), 3.42 (t, 2H), 3.60-3.88, (m, AB system, 4H), 3.90-4.20 (m, AB system, 10H), 7.00-7.11 (m, 2H), 7.25 (d, 1H), 7.30-7.45 (m, AB system, 4H), 7.60 (d, 1H), 7.75-7.85 (m, 2H), 8.78 (d, 2H), 8.87 (d, 2H) 13.62 (d, H), 14.2 (d, H). ^{13}C NMR (100 MHz, CD_3CN), δ (ppm): 25.11, 26.14, 45.17, 47.79, 48.01, 51.50, 51.78, 55.95, 55.98, 56.85, 57.01, 59.29, 104.64, 105.74, 121.68, 121.86, 123.62, 123.84, 125.46, 129.49, 131.51, 135.15, 136.48, 139.42, 139.49, 139.58, 142.35, 148.47, 148.56, 15.11; 150.26; 155.75, 146.30, 164.53, 168.53, 171.80.

$[Zn^{II}L^3(H^+)_2](ClO_4)_2 \cdot 2H_2O$, 6: to a stirred solution of $[Zn^{II}L^2(H^+)_2](ClO_4)_2 \cdot H_2O$, 5, (500 mg, 0.48 mmol) in CH_3CN (5 mL) at 0° C was added dropwise over 60 min a solution of $NaBH_4$ (25 mg, 0.66 mmol) in acetonitrile (3 mL). The intense yellow color of the imine disappeared rather abruptly near the end of the addition. The resultant colorless solution was warmed to 25° C over 60 min. Acetic acid (222 μL, 3.89 mmol) was then added to the reaction mixture and a small amount of gas evolution was observed. To the solution was added water (2 mL) that resulted in the formation of yellow solid. The total volume of the mixture was reduced to 5 mL under reduced pressure. The solid was collected, washed with EtOH (2 × 10 mL), Et_2O (2 × 5 mL) and *n*-Hexane (2 × 5 mL) and dried under vacuum. The crude compound was recrystallized by diffusion of diethyl ether into

CH$_3$CN solution. Yielded 31 mg, 69%. Anal. calcd. for C$_{36}$H$_{45}$N$_7$O$_{10}$Br$_2$Cl$_2$Zn·2H$_2$O (M$_w$ = 1067.91 g. mol^{-1}) (%): C, 40.49; H, 4.62; N, 9.18. Found: C, 40.02; H, 4.04; N, 9.30. FT–IR (KBr, cm^{-1}): 3501 and 3360 (b, N-H), 3071 (m, C-H), 2929 (m, C-H), 1607(s), 1436 (s, Ph-O), 1241 (s), 1095 (s, ClO$_4$), 624 (m, ClO$_4$). ^{1}H NMR (400 MHz, CD$_3$CN), δ (ppm): 2.70-3.00 (AB system, 10H); 3.10-3.30 (m, 7H); 3.45 (d, 2H); 3.55 (m, 2H,); 3.80, 4.10 (AB syst, 10H); 7.10 (m, 6H,); 7.35 (m, 2H); 7.80 (m, 2H); 8.85 (d, 2H), 13.7 d, H), 14,1 (d, H). ^{13}C NMR (100 MHz, CD$_3$CN), δ (ppm): 23.83; 26.27; 45.25; 47.47; 48.56; 51.16; 51.25; 56.84, 57.07; 57.86; 60.89; 61.94; 104.72; 105.29; 122.31; 122.37; 122.57; 123.22; 124.54; 124.65; 126.39; 126.83; 132.48; 133.33; 134.01; 135.49; 136.03; 140.22; 149.47; 149.59; 157.26; 157.48; 165.48; 165.88.

[Zn^{II}L^{2}Cu^{II}](ClO$_4$)$_2$·H$_2$O, 7: to a solution of [Zn^{II}L^2(H$^+$)$_2$](ClO$_4$)$_2$·H$_2$O, 5 (200 mg, 0.195 mmol) in CH$_3$CN (5 mL) was added dropwise a solution of Cu(ClO$_4$)$_2$·6H$_2$O (72 mg, 0.195 mmol) in acetonitrile (5 mL) and Et$_3$N (0.055 mL, 0.390 mmol) in acetonitrile (1.5 mL) over 5 min. The brown mixture was stirred for 30 min and a filtrated saturated solution of NH$_4$ClO$_4$ (600 mg, 3.3 mmol) in acetonitrile (3 mL) was then added to the resulting solution. The solution was partially concentrated at room temperature to reduce the CH$_3$CN content; diethyl ether was then added (10 mL) and the solution was allowed to stand overnight. The resultant brown solid was collected and washed with ethanol (2 × 2 mL), Et$_2$O (2 × 2 mL) and n-hexane (2 × 2 mL). The crude compound was recrystallized by diffusion of Et$_2$O into the CH$_3$CN solution. Typical yield 84%. Anal. calcd. for C$_{36}$H$_{39}$N$_7$O$_{10}$Cl$_2$Br$_2$ZnCu·H$_2$O (M$_w$ = 1107.39 g. mol^{-1}) (%): C, 39.05; H, 3.73; N, 8.85. Found: C, 39.30; H, 3.74; N, 8.86. FT–IR (KBr, cm^{-1}): 3443 (b, N-H), 32.41 (m, C-H), 2927 (m, C-H), 1624 (s, C=N), 1606(s, C=C), 1435 (s, Ph-O), 1092 (s, ClO$_4$), 624(m, ClO$_4$).

[Zn^{II}L^{3}Cu^{II}](ClO$_4$)$_2$·H$_2$O, 8: this compound was prepared with the same procedure as for [Zn^{II}L^{2}Cu](ClO$_4$)$_2$·H$_2$O except that [Zn^{II}L^3(H$^+$)$_2$](ClO$_4$)$_2$·H$_2$O, 6 was used as starting material instead of [Zn^{II}L^2(H$^+$)$_2$](ClO$_4$)$_2$·H$_2$O . Typical yield 87%. Anal. calcd. for C$_{36}$H$_{43}$N$_7$O$_{10}$Cl$_2$Br$_2$ZnCu·H$_2$O (M$_w$ = 1111.42 g. mol^{-1}) (%): C, 38.90; H, 4.08; N, 8.82. Found: C, 38.77; H, 4.02; N, 8.96. FT–IR (KBr, cm^{-1}): 3445 and 3366 (b, N-H), 32.41 (m, C-H), 2927 (m, C-H), 1606 (s, C=C), 1438 (s, Ph-O), 1093 (s, ClO$_4$), 624 (m, ClO$_4$).

3. Results and discussion
3.1. Synthesis
The heterodinuclear complexes were prepared according with consequence of steps presented in Scheme 2. In this regard, dialdehyde [ZnL^1] complex that its structure was characterized previously, as trans-disposed pyridyl ligand with C_2 symmetrical geometry, was used as a starting material [20].The mononuclear macrocyclic [ZnL^2(H$^+$)$_2$](ClO$_4$)$_2$·H$_2$O, **5** complex was prepared by the condensation of the [ZnL^1], **4** with an equivalent of dipropylenetriamine in ethanol followed by addition of a saturated solution of ammonium perchlorate. The corresponding mononuclear amine complex of [Zn^{II}L^3(H$^+$)$_2$](ClO$_4$)$_2$·H$_2$O, **6** was prepared by BH$_4^-$ reduction of [Zn^{II}L^2(H$^+$)$_2$](ClO$_4$)$_2$·H$_2$O, **5** as pale yellow solid. Subsequently, the resultant macrocyclic zinc complexes were dissolved in acetonitrile and copper(II) ion was introduced in the

presence of a base to remove two protons in the N_3O_2 coordination site.

Under these reaction conditions the heterodinuclear macrocyclic complexes [$Zn^{II}L^2Cu^{II}$](ClO$_4$)$_2 \cdot$H$_2$O, **7** and [$Zn^{II}L^3Cu^{II}$](ClO$_4$)$_2 \cdot$H$_2$O, **8** were prepared with moderate yield. The characterization results indicate that the mononuclear macrocyclic complexes [$Zn^{II}L^2(H^+)_2$](ClO$_4$)$_2 \cdot$H$_2$O, **5** and [$Zn^{II}L^3(H^+)_2$](ClO$_4$)$_2 \cdot$H$_2$O, **6** have *trans* pyridyl geometry but upon introduction of the second metal ion, into the O_2N_3-coordination site, leads to formation of a structure where two pyridyl ligands are cis–disposed. The unsymmetrical structure arises from small chelate ring size and the conformations that ligand adapts. In the mononuclear complexes the ethylenediamine chelate bite angle in the N_4O_2-coordination site is less than 90° causing the *trans* phenolate-O-Zn-O-phenolate angle to expand beyond a value that can accommodate the second contiguous metal ion [19,20,22]. Thus, in order to accommodate the second metal ion into the N_2O_2 compartment the O-Zn-O angle requires to be reduced which causes the phenolate moieties to buckle to the same side of the mean macro-acyclic plane. This buckling forces the pyridyl ligands to be *cis*-disposed on the other side of the mean macro-acyclic plane [20,22].
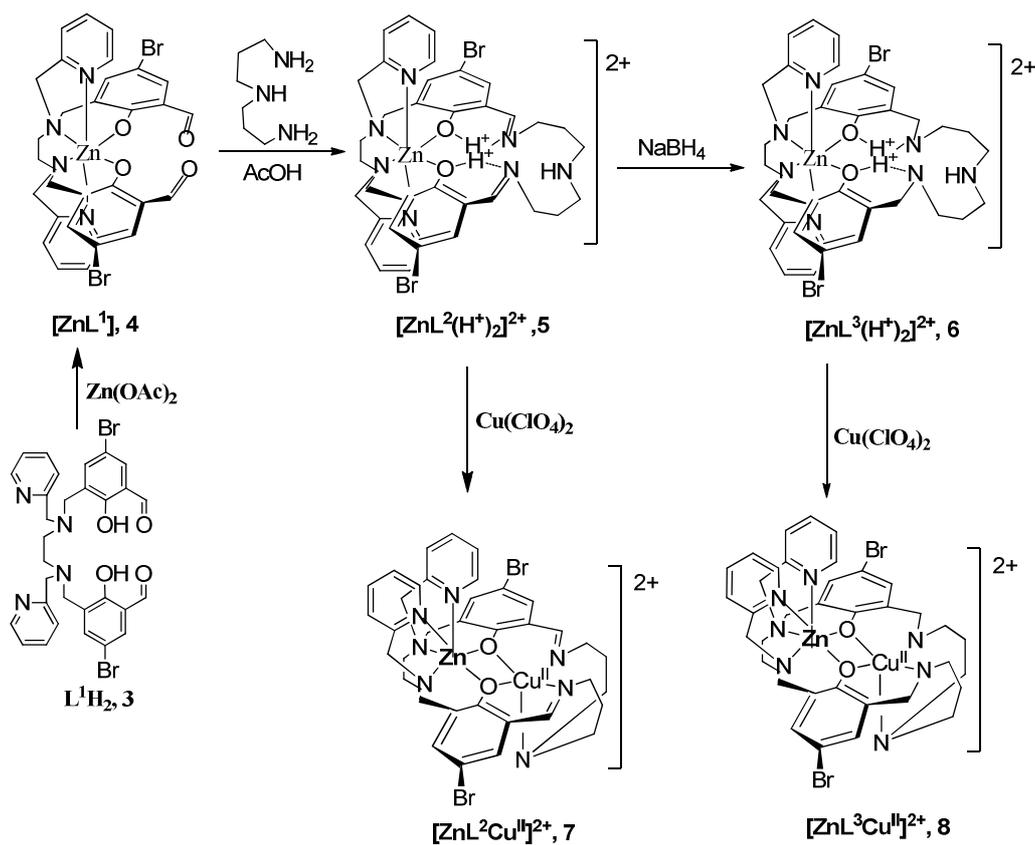
Scheme 2. Synthetic scheme for the mono- and dinuclear macrocyclic complexes.

3.2. Characterization

Conductometric data: the molar conductance values of the mono- and heterodinuclear complexes measured in acetonitrile solution at 25°C are presented in Table 1.

The values are accurate to $\pm$ 5 Ω^{-1} cm^2 mol^{-1}. The results are in agreement with the expected range of the values for 3-ion electrolytes and consistent with their formulas. Three-ion electrolytes observed in mononuclear complexes are due to the present of two protons in the O_2N_3 cavity, which resulted in formation of a doubly charged complex, $[Zn^{II}L^3(H^+)_2]^{2+}$, 6, and presence of two perchlorate anions as counter ions.

Table 1. Molar conductivities data of the complexes in solvent of acetonitrile [a].

Compound	Λ_m of the complexes (Ω^{-1}cm^2 mol^{-1}, at 25° C)
$[ZnL^2(H^+)_2](ClO_4)_2$	234
$[ZnL^3(H^+)_2](ClO_4)_2$	231
$[ZnL^2Cu^{II}](ClO_4)_2$	222
$[ZnL^3Cu^{II}](ClO_4)_2$	228
1:2 electrolytes	220-300

[a.] Concentration: ca.1.0×10^{-3} M.

Electronic absorption spectra: the electronic absorption spectra of the mono- and dinuclear complexes were recorded in acetonitrile solutions over the range 200 – 900 nm. These regions include d-d transition and some of the metal-ligand charge transfer bands.

The characteristic features in all mono and dinuclear macrocyclic complexes consist of intense absorption bands at around 300 nm due to phenolate-zinc charge transfer (LMCT) [27].

This band loses its intensity in dinuclear complexes. The intense band at 402 nm in macrocyclic complex of $[Zn^{II}L^2(H^+)_2](ClO_4)_2$,5 is assigned to the $\pi - \pi*$ transition associated with the azomethine linkages [28]. This band in $[Zn^{II}L^2Cu^{II}](ClO_4)_2$,7, shifted to the lower wavelength due to coordination to copper(II) ion. In the low energy region the $[Zn^{II}L^2Cu^{II}](ClO_4)_2$, 7, and $[Zn^{II}L^3Cu^{II}](ClO_4)_2$ 8, demonstrated a bands at around 640 nm which is attributed to the d-d transitions of the copper(II) ion in a square pyramidal environment [29]. Table 2 lists the positions and intensities of the phenolate charge-transfer and the d-d bands observed in the spectra of the complexes.

Table 2: Electronic spectral data for mono- and heterodinuclear complexes in acetonitrile solutions.

Complex	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	
	C. T.	d-d
$[ZnL^2(H^+)_2](ClO_4)_{2,}$ **5**	307 (8034) 402 (12337) 498 (1304)	-
$[ZnL^3(H^+)_2](ClO_4)_{2,}$ **6**	305 (7915)	- - -
$[ZnL^2Cu^{II}](ClO_4)_{2,}$ **7**	298 (2369) 369 (6904)	640 (122)
$[ZnL^3Cu^{II}](ClO_4)_{2,}$ **8**	296 (1023) 370 (1751)	642 (101)

Infrared spectra: The infrared spectra of the mononuclear dialdehyde $[ZnL^1]$ and diimine $[ZnL^2(H^+)_2](ClO_4)_2$, 5, complexes are very similar. Significant differences between the dialdehyde and diimine complexes in the spectra are the emergence of a sharp, but weak, band at about 3436 cm^{-1}, which is attributed to the N-H stretch of the amine moiety of dipropylenetriamine link [30], and the appearance of strong bands at about 1094 cm^{-1} and 623 cm^{-1}, corresponding to the anti-symmetric stretching and anti-symmetric bending vibration modes of perchlorate ions, respectively [31]. Strong evidence that the aldehyde groups had been completely converted into imine groups was provided by the disappearance of the aldehydic C=O stretching band at around 1670 cm^{-1} and the appearance of a strong band at around 1651 cm^{-1} assigned to C=N stretching vibration mode [32,33]. Appearance of a band near 1435 cm^{-1} for all of the complexes is assigned to the skeletal vibration of the aromatic rings [34].

The infrared spectra of the diimine compounds and its amine counterparts are generally similar but at the same time complicated. The major differences in the spectra between the imines and amines are the appearance of another broad but weak band at 3360 cm^{-1} which is attributed to the N-H stretch of the

quaternized amine of the –NH moiety of dipropylenetriamine link (-NH-CH$_2$Ph) [35], and the disappearances of the strong band at 1651 cm^{-1}, corresponding to the C=N stretch of the imine groups [30]. Appearance of a band near 1435 cm^{-1} for all of the complexes is assigned to the skeletal vibration of the aromatic rings [36.

NMR spectra: the ^{1}H NMR spectrum of the mononuclear macrocyclic complexes in CD$_3$CN reveals two protons at 13.7 and 14.2 ppm.

These signals are assigned to the open-site protons. The azomethine protons of [Zn^{II}L^2(H$^+$)$_2$](ClO$_4$)$_2$, 5, at 8.78 and 8.87 ppm (J = 5.0 Hz) are split by coupling to these protons. Addition of D$_2$O to the NMR sample causes rapid proton-deuterium exchange as evidenced by the disappearance of the proton signals and the absence of detectable coupling to the azomethine protons. The presence of a plethora of signals in ^{1}H NMR and ^{13}C NMR spectra of [ZnL^2(H$^+$)$_2$](ClO$_4$)$_2$, 5, and [ZnL^3(H$^+$)$_2$](ClO$_4$)$_2$, 6, suggests that both molecules possess a unsymmetrical C_I symmetric structure. This is perhaps due to the presence of dipropylenetriamine link in the O$_2$N$_3$ coordination site and lack of its flexibility in solution. The structures of their analogous compounds were established by x-ray crystallography [19,22] that confirms the structure shown in Scheme 2.

4. Conclusion

The dinucleating macrocyclic compartmental ligand, derived from the condensation of dialdehyde Zn(II) complex with dipropylenetriamine have been prepared. In the mononuclear complexes the macrocyclic ligands have the normal structure with *trans*-disposed pyridyl ligands and two protons are located in the O$_2$N$_3$ coordination site. However the dinuclear complexes showed abnormal structures in which the two pyridyl ligands disposed themselves in a *cis* position around the zinc atom and the Cu(II) ion occupied the O$_2$N$_3$ coordination site with square pyramidal geometry.

5. References

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