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# Two novel macroacyclic schiff bases containing bis-N<sub>2</sub>O<sub>2</sub> donor set and their binuclear complexes: synthesis, spectroscopic and magnetic properties

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# ABSTRACT

Herein, we report two novel macroacyclic Schiff bases derived from tetranaphthaldehyde derivative compound and their binuclear Mn(II), Ni(II), Cu(II) and Zn(II) complexes. The structures of the compounds have been proposed by elemental analyses, spectroscopic data i.e. IR, <sup>1</sup>H and <sup>13</sup>C NMR, UV–Vis, electrospray ionisation mass spectra, molar conductivities and magnetic susceptibility measurements. The stoichiometries of the complexes derived from mass and elemental analysis correspond to the general formula  $[M_2L(CIO_4)_n](CIO_4)_{4-n}$ , (where M is Mn(II), Ni(II), Cu(II), Zn(II) and L represents the Schiff base ligands).

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# 1. Introduction

Schiff bases can form coordinate bond with the transition metal atom ion via nitrogen atom of C=N- double bond, and with an ortho-position oxygen(O) or sulfur(S) atom which have a lonely pair of electrons. Schiff base complexes have specific activities of pharmacology and physiology [1a,b]. They have wide applications in various fields such as illness treatment, biochemical reaction and biological regulator and have been studied for their interesting and important properties, [1c,2–5]. Therefore, people pay a great interest in their synthesis, structure, biological activity and application of this kind of complexes [6–8].

2-Hydroxy Schiff base ligands and their complexes derived from the reaction of salicylaldehyde and 2-hydroxy-1-naphthaldehyde derivatives with amines have been extensively studied [9–14] and a number of them were used as models for biological systems [15–19]. In addition, a large number of dinuclear complexes have been synthesized and structurally characterized in attempts to mimic the active sites of metallo-enzymes [20–22].

There have been numerous transition metal complexes containing  $N_2S_2$  or  $N_2O_2$  donor set [23,24] but only a few examples of complexes containing a bis- $N_2O_2$  donor set have been reported in the literature [25].

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In view of these finding and in continuation to our previous work on the Schiff bases [26], this work has devoted with the aim to synthesize some homo-dinuclear Mn(II), Ni(II), Cu(II) and Zn(II) complexes with two novel macroacyclic Schiff bases ligands (Fig. 1), and to examine their physical properties involving spectral behaviors by IR, <sup>1</sup>H and <sup>13</sup>C NMR, UV–Vis, electrospray ionisation mass spectra, molar conductivities and magnetic moment data. A detailed assignment of the spectra and the electrochemical behavior were proposed.

# 2. Experimental

# 2.1. Physical measurements

Melting points (m.p.) were determined on a Barnstead/Electrothermal 9100 apparatus in open capillary tubes. IR spectra were recorded on a Perkin Elmer Spectrum 100 FTIR spectrophotometer as KBr pellets. <sup>1</sup>H and <sup>13</sup>C NMR. spectra were recorded on a Varian Gemini 200 and Varian Mercury 400 spectrometer using chloroform-d<sub>1</sub>/DMSO-d<sub>6</sub> solvents at Department of Chemistry, Karadeniz Technical University, Trabzon and Ataturk University, Erzurum, respectively. Chemical shifts ( $\delta$ ) are reported in part per million (ppm) relative to an internal standard of Me<sub>4</sub>Si. A Shimadzu 1601-PC UV/Vis spectrophotometer was used to record the electronic spectra. Room temperature (296 K) solid state magnetic susceptibilities were measured by using a Sherwood Scientific magnetic susceptibility balance and MnCl<sub>2</sub>.6H<sub>2</sub>O was used as the standard.

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Fig. 1. Synthesis pathway for ligands synthesis.

Elemental analyses were determined on a LECO CHNSO-932 auto elemental analyses apparatus. Metal containing of the complexes were determined by atomic absorption (Unicam 929) spectral techniques using standard flames [27] and electrospray ionisation mass spectrometry (ESI-MS) was performed on a VG 7070 spectrometer at Department of Chemistry, Karadeniz Technical University, Trabzon, Turkey. Solution electrical conductivities were measured at r.t. with approximately  $10^{-3}$  M DMF solutions, with a Hanna EC 215 conductivity meter by using 0.01 M KCl water solution as calibrant.

# 2.2. Materials

2-Hydroxy-1-naphthaldehyde, 2,3-dimethyl-1,3-butadiene obtained from Fluka. The perchlorate salts of Mn(II), Ni(II), Zn(II), Cu(II), bromine, aniline and methyl amine were purchased from Merck. 2,2'-[2,3-Bis(1-formyl-2-naphthyloxymethyl)-but-2-ene-1,4-diyldioxy]bis(naphthalene-1-carbaldehyde) were synthesized according to the procedure [28]. Organic solvents were reagent grade chemicals.

#### Table 1

Analytical and physical data of Schiff bases and their complexes.

Compound	Color	Yield (%)	M.p. (°C)	[M <sup>+</sup> ]	µ <sub>eff</sub> per metal	$\Lambda^{\rm f}$	Found (Calcd.) (%)			
					1011 at 200 it (2111)		С	Н	Ν	М
L <sup>1</sup> , ( <b>2</b> )	Yellow	83	183	1065 <sup>b</sup>	-	-	82.9 (83.4)	5.2 (5.3)	5.4 (5.3)	-
C <sub>74</sub> H <sub>56</sub> N <sub>4</sub> O <sub>4</sub>										
$[Mn_2L^1(ClO_4)_4], (3)$	Brown	56	190	1572.26 <sup>b</sup>	5,27	10	56.7 (56.5)	3.8 (3.6)	3.5 (3.6)	7.3 (7.0)
C <sub>74</sub> H <sub>56</sub> Cl <sub>4</sub> Mn <sub>2</sub> N <sub>4</sub> O <sub>20</sub>										
$[Ni_2L^1(ClO_4)_4], (4)$	Brown	66	122	1582.50 <sup>c</sup>	2,45	20	55.9 (56.2)	3.6 (3.6)	3.4 (3.6)	7.2 (7.4)
C <sub>74</sub> H <sub>56</sub> Cl <sub>4</sub> N <sub>4</sub> Ni <sub>2</sub> O <sub>20</sub>										
$[Cu_2L^1(ClO_4)_4], (5)$	Dark green	67	188	1590.14 <sup>b</sup>	1,88	63	56.3 (55.9)	3.7 (3.6)	3.7 (3.5)	7.9 (8.0)
C <sub>74</sub> H <sub>56</sub> Cl <sub>4</sub> Cu <sub>2</sub> N <sub>4</sub> O <sub>20</sub>										
$[Zn_2L^1(ClO_4)_4], (6)$	Light yellow	65	201	1596.74 <sup>d</sup>	Diamagnetic	2	56.1 (55.8)	3.6 (3.5)	3.8 (3.5)	8.1 (8.2)
C <sub>74</sub> H <sub>56</sub> Cl <sub>4</sub> N <sub>4</sub> O <sub>20</sub> Zn <sub>2</sub>										
L <sup>2</sup> , ( <b>7</b> )	Light yellow	62	184	817.42 <sup>b</sup>	-	-	80.0 (79.4)	6.0 (5.9)	6.9 (6.9)	-
C <sub>54</sub> H <sub>48</sub> N <sub>4</sub> O <sub>4</sub>										
$[Mn_2L^2(ClO_4)_4], (8)$	Light brown	34	200	1324.68 <sup>b</sup>	3,79	42	48.4 (49.0)	3.8 (3.6)	4.4 (4.2)	8.2 (8.3)
C <sub>54</sub> H <sub>48</sub> Cl <sub>4</sub> Mn <sub>2</sub> N <sub>4</sub> O <sub>20</sub>										
$[Ni_2L^2(ClO_4)_4], (9)$	Light green	58	249 <sup>a</sup>	1334.18 <sup>c</sup>	2,96	9	49.0 (48.7)	3.7 (3.6)	4.0 (4.2)	9.0 (8.8)
C <sub>54</sub> H <sub>48</sub> Cl <sub>4</sub> N <sub>4</sub> Ni <sub>2</sub> O <sub>20</sub>										
$[Cu_2L^2(ClO_4)_2](ClO_4)_2$ , ( <b>10</b> )	Green	52	255 <sup>ª</sup>	1179.4 <sup>e</sup>	1,90	120	47.9 (48.3)	3.4 (3.6)	4.1 (4.2)	9.8 (9.5)
C <sub>54</sub> H <sub>48</sub> Cl <sub>4</sub> Cu <sub>2</sub> N <sub>4</sub> O <sub>20</sub>										
$[Zn_2L^2(ClO_4)_2](ClO_4)_2, (11) C_{54} H_{48} Cl_4 N_4 Zn_2 O_{20}$	Light yellow	62	215	1146.5 <sup>f</sup>	Diamagnetic	172	48.1 (48.2)	3.7 (3.6)	4.2 (4.2)	9.9 (9.7)

<sup>a</sup> Decomposition.

<sup>b</sup> [M]<sup>+</sup>.

<sup>c</sup> [M+2]<sup>+</sup>

<sup>d</sup> [M+3)]<sup>+</sup>.

 $^{e}$  [M+2H<sub>2</sub>O-2ClO<sub>4</sub>+1]<sup>+</sup>.

<sup>f</sup> [M-2ClO<sub>4</sub>+1]<sup>+</sup>. Molar conductivities were measured in DMF solvent with concentration  $\times$  10<sup>-3</sup> M. Values are in ( $\Omega^{-1}$  mol<sup>-1</sup> cm<sup>2</sup>).

**Caution!** perchlorates and perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared and it should be handled with care.

# 2.3. Synthesis of ligands

2.3.1. Synthesis of phenyl{(1E)-[2-({4-({1-[(E)-(phenylimino)methyl]-2-naphthyl}oxy)-2,3-bis[({1-[(E)-(phenylimino)methyl]-2-naphthyl}oxy) methyl]but-2-en-1-yl}oxy)-1-naphthyl]methylene}amine, L<sup>1</sup>, (**2**)

The ligand was prepared by refluxing equimolar amounts of the 2,2'-[2,3-Bis(1-formyl-2-naphthyloxymethyl)-but-2-ene-1,4-diyldi-

oxy]bis(naphthalene-1-carbaldehyde), (1) (2 g, 2,6 mmol) with aniline (10,4 mmol; 1.05 cm<sup>3</sup>) for 60 h, THF used as solvent. Reaction was monitored by TLC using chloroform–ethanol (40:1). Upon cooling, solvent was removed by rotary. Obtained yellow product was refluxed in ethanol 1 h, then filtered off and washed with warm ethanol several times, dried in the oven; M.p. 148 °C, 83% yield.

# 2.3.2. Synthesis of methyl{(1E)-[2-(4-((1-[(E)-(methylimino)methyl]-2-naphthyl}oxy)-2,3-bis[( $\{1$ -[(E)-(methylimino)methyl]-2-naphthyl} oxy)methyl]but-2-en-1-yl}oxy)-1-naphthyl]methylene}amine, $L^2$ , (**3**)

The ligand was prepared by stirring of the 2,2'-[2,3-Bis(1-formyl-2-naphthyloxymethyl)-but-2-ene-1,4-diyldioxy]bis(naphtha-



Fig. 2. Proposed structure of the homo-dinuclear complexes.

#### Table 2

Characteristic IR bands of the Schiff bases and their metal complexes (in cm<sup>-1</sup>).

Compound	v (C=O)	v (C=C)	v (C=N)	v (C—O)	v (ClO <sub>4</sub> ) <sup>-</sup>	Mono substitute phenyl	$v_{M-O}$	v <sub>M-N</sub>
Tetraaldehyde ( <b>1</b> )	1673 s	1619 m, 1591 m	-	1238, 1208	-	-	-	-
$L^{1}$ , ( <b>2</b> )	-	1624 m, 1586 s	1608 m	1239 s, 1208 s	-	694 m, 766 m	-	-
$[Mn_2L^1(ClO_4)_4], (3)$	-	1622 m, 1588	1673 s	1236 s, 1211 s	1069 brs, 621 w	694 w, 749 m	574	506
$[Ni_2L^1(ClO_4)_4], (4)$	-	1622 m, 1587 s	1674 s	1239	1050,1075, 1118 m, 622 w	694 m, 748 s	571 w	507
$[Cu_2L^1(ClO_4)_4], (5)$	-	1618 m, 1590 s	1674 s	1239 s	1089, 1102, 1121 brm, 621w	709 w, 751 m	570 w	501
$[Zn_2L^1(ClO_4)_4], (6)$	-	1619 m, 1590 s	1674 s	1239 s	1088 m	708 w, 752 m	570 w	506
L <sup>2</sup> , ( <b>7</b> )	-	1615 m, 1588 m	1639 m	1211 s, 1234 s	-	-	-	-
$[Mn_2L^2(ClO_4)_4], (8)$	-	1619 m, 1519 s	1672 s	1239 s, 1230	1093 brs, 623 m	-	570	520
$[Ni_2L^2(ClO_4)_4], (9)$	-	1619 s, 1591 s	1674 s	1239 s, 1231 s	1067 brm, 627 m	-	570	504
$[Cu_2L^2(ClO_4)_2](ClO_4)_2$ , (10)	-	1619 s, 1590 s	1671	1238 s	1086 brs, 624 s	-	567	503
$[Zn_2L^2(ClO_4)_2](ClO_4)_2$ , (11)	-	1620 m, 1590 m	1663 s	1206 m,1238 s	1089, 1105, 1147 brs, 625 s	-	-	-

s, sharp; m, medium; br, broad; w, weak.

#### Table 3

<sup>1</sup>H and <sup>13</sup>C NMR spectral data of the Schiff bases in CDCl<sub>3</sub>.

<sup>1</sup> H data for <i>L</i> <sup>1</sup>	<sup>13</sup> C data for L <sup>1</sup>		<sup>1</sup> H data for $L^2$	<sup>13</sup> C data for L <sup>2</sup>	
5.05 s. (-OCH <sub>2</sub> -, 8H),	C-1	135.484	3.407-3.404 s. (CH <sub>3</sub> -, 12H),	C-1	136.069
7.212-6.994 m. (Ar, 24H)	C-2	66.627	5.115 s. (-OCH <sub>2</sub> -, 8H),	C-2	66.983
7.442, 7.404, 7.368 t. (Ar, 4H)	C-3	157.584	7.278 <sup>*</sup> (Ar, 4H)	C-3	156.449
7.716, 7.523 m. (Ar, 12H)	C-4	118.156	7.409, 7.390, 7.371 t (Ar, 4H)	C-4	119.128
9.072 s. (-HC=N, 4H)	C-5	133.761	7.539, 7.521, 7.501 t (Ar, 4H)	C-5	132.289
9.327–9.286 d. (Ar, 4H)	C-6	129.543	7.754, 7.734 d (Ar, 4H)	C-6	129.853
	C-7	128.549	7.809, 7.786 d (Ar, 4H, J = 9.16)	C-7	128.312
	C-8	124.673	8.877 s. (-HC=N, 4H,)	C-8	124.714
	C-9	125.659	9.004, 8.982 d. (Ar, 4H, J = 8.8)	C-9	125.837
	C-10	125.826		C-10	128.259
	C-11	131.857		C-11	132.547
	C-12	113.550		C-12	114.187
	C-13	157.637		C-13	159.674
	C-14	152.766		C-14	49.761
	15	120.758			
	C-16	129.050			
	C-17	128.299			

\* The signal collides with signal of solvent proton and is probable a doublet.

lene-1-carbaldehyde), (1) (2 g, 2,6 mmol) with excessive amount of methyl amine solution (5 cm<sup>3</sup>, 41%) for a week at room temperature. Reaction was monitored by TLC using chloroform–ethanol (40:1). Obtained solid product was washed with water, cold ethanol and diethyl ether several times, dried in the oven; M.p. 184 °C, 62% yield.

# 2.4. Synthesis of metal complexes $[M_2L^1(ClO_4)_n](ClO_4)_{4-n}$ , $[M_2L^2(ClO_4)_n](ClO_4)_{4-n}$

The metal complexes of the Schiff bases were prepared by the addition of hot solution (40 °C) of the metal perchlarate (0.4 mmol) [Cu (ClO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O, Ni(ClO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O, Zn(ClO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O or Mn(ClO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O] in 10 mL ethanol to the hot solution (40 °C) of Schiff base (0.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL). The resulting mixture was stirred for 6 h under

Table 4

 $^{1}$ H NMR spectral data of the [Zn<sub>2</sub>L<sup>1</sup>(ClO<sub>4</sub>)<sub>4</sub>], (6) and [Zn<sub>2</sub>L<sup>2</sup>(ClO<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, (11).

<sup>1</sup> H data for <b>6</b> in $CDCl_3$	<sup>1</sup> H data for <b>11</b> in DMSO-d <sub>6</sub>
10.833 s(—HC=N, 4H) 9.084, 9.105 d. (H <sup>10</sup> , 4H, J = 8.4 Hz)	10.651 s(-HC=N, 2H) and 8.766 bs .(-HC=N, 2H) 9.098, 9.077 d. (H <sup>10</sup> , 2H, <i>J</i> = 8.4 Hz) and 8.978, 8.957 d. (H <sup>10</sup> , 2H, <i>J</i> = 8.4 Hz)
8.034, 8.012 d. (H <sup>5</sup> , 4H, <i>J</i> = 8.8 Hz)	8.238, 8.215 d. (H <sup>5</sup> , 2H, <i>J</i> = 9.2 Hz) 7.994, 7.971 d. (H <sup>5</sup> , 2H, <i>J</i> = 9.2 Hz)
7.755, 7.734 d. (H <sup>7</sup> , 4H, <i>J</i> = 8.4 Hz)	7.915, 7.895 d. (H <sup>7</sup> , 2H, <i>J</i> = 8.0), 7.876, 7.856 d. (H <sup>7</sup> , 2H, <i>J</i> = 8.0 Hz),
7.605, 7.602, 7.584 t. (H <sup>9</sup> , 4H)	7.745, 7.719 d. (H <sup>4</sup> , 2H, <i>J</i> = 10.4 Hz),
7.567, 7.563, 7.520 t. (H <sup>8</sup> , 4H)	7.645–7.565 m. (H <sup>8, 9</sup> , 4H), and 7.513–7.387 m. (H <sup>4, 8, 9</sup> , 6H)
7.433–7.261 m. (H <sup>15, 17</sup> , 8H)	5, 414 and 5.280 s. (H <sup>2</sup> , 8H)
7.177, 7.158, 7.137 t. (H <sup>16</sup> , 4H)	3.100 <sup>*</sup> s. (H <sup>14</sup> , 6H)
6.681, 6.700 d. (H <sup>4</sup> , 4H, J = 7.6 Hz)	
5.219 s. (H <sup>2</sup> , 8H)	

The other singlet were hindered by H<sub>2</sub>O protons of solvent.

reflux and the mixture stirred for overnight at room temperature. After the reaction was complete, the solvent was removed from the reaction mixture to 10 mL volume in vacuo. 50 mL of distilled water:ethanol(1:1) was poured into the reaction mixture with vigorous stirring and precipitate was produced. The solid metal complexes having 2:1 metal:ligand ratio were collected by filtration, washed with water, ethyl alcohol and diethyl ether, respectively, and dried over silica gel in vacuo.

# 3. Results and discussion

Analytical and physical data of Schiff bases and their complexes are presented in Table 1. Macroacyclic Schiff bases were synthesized by the condensation of 2,2'-[2,3-bis(1-formyl-2-naphtyloxymethyl)but-2-ene-1,4-diyldioxy]bis(naphthalene-1-carbaldehyde), (1) with aliphatic and aromatic primer amines in 1:4 molar ratio in THF or CHCl<sub>3</sub>. The structures of Schiff bases were characterized by using elemental analysis (C, H, N), <sup>1</sup>H and <sup>13</sup>C NMR, IR and mass spectral data. In the proposed structure of the Schiff base ligands have bis-N2O2 cores to form dinuclear metal complexes. The stoichiometries of the complexes derived from mass and elemental analysis correspond to the general formula  $[M_2L(ClO_4)_n](ClO_4)_{4-n}$ , (where M is Mn(II), Ni(II), Cu(II), Zn(II) and L is the Schiff base ligand). Proposed structures of the homo-dinuclear complexes are shown in Fig. 2. These propositions are also in accord with IR, UV-Vis data, magnetic and molar conductivity measurements. The vellow-coloured Schiff base  $(L^1)$  is soluble in CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, DMF, DMSO, pyridine but insoluble in water, ethanol, methanol. The light yellow-coloured Schiff base  $(L^2)$  is soluble in CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, DMF, DMSO, pyridine but insoluble in water, ethanol, methanol and all the complexes are soluble in DMF, DMSO and pyridine.

# 3.1. NMR spectra

<sup>1</sup>H NMR spectra of Schiff base ligands were recorded in CDCl<sub>3</sub> solution. These <sup>1</sup>H NMR results are presented in Table 3 (see



Fig. 3. The mass spectrum of  $[Zn_2L^1(ClO_4)_4]$ .

Fig. 1 for the numbering scheme). The singlet at  $\delta$  10.67 ppm belonging to tetraaldehyde protons of (1) disappears after the reaction of the aniline and methylamine with the tetra aldehyde and a new singlet at 9.072 ppm for  $L^1$ , 8.877 ppm for  $L^2$  correspond to the N=CH proton resonances. More detailed information about the structure of Schiff bases ( $L^1$  and  $L^2$ ) is provided by its <sup>13</sup>C NMR spectrum. In the spectrum of Schiff bases were observed disappearing the carbonyl carbon signal of tetraaldehyde (1) at 190.72 ppm, a new signal at 157.634 ppm for  $L^1$  and 156.974 ppm for  $L^2$  due to imine carbon (C=N), a shift for the carbon of O–Ar from 162.84 to 157.584 for  $L^1$  and 156.449 ppm for  $L^2$ . These observations are an evidence formation of Schiff bases.

<sup>1</sup>H NMR spectra of Zn(II) complexes (**6**, **11**) were recorded in CDCl<sub>3</sub> and DMDO-d<sub>6</sub> solution, respectively (Table 4). The <sup>1</sup>H NMR spectrum of the Zn(II) complexes were compared with the parent Schiff bases. In the <sup>1</sup>H NMR spectrum of **11**, each of H(2) and, H(13) protons appear as two different singlets and each of H(4), H(5), H(7), H(14) appear as two different doublets, each of H(8), H(9) appear as two different triplets as a consequence of low molecular symmetry of **11**. But, the triplets from H(8), H(9) protons and one of the doublets of H(4) protons appear as two different multiplets since they collide with each other. The resonance due

to azomethine protons in the complexes appear at 10.833 as a singlet for **6** and two singlets at 10.651, 8.766 ppm, for **11**. The resonance due to O—CH<sub>2</sub>, (H2) protons appear at 5.219 ppm as a singlet for **6** and at 5.414 and 5.280 ppm as two different singlets for **11**. The observation of downfield/highfield shifts indicate the coordination of imine nitrogen and phenolic oxygen atoms to Zinc(II) ions.

#### 3.2. IR spectra and mode of bonding

IR spectra give enough information to elucidate the way of bonding of the ligands to the metal ions. The main vibration frequencies of the ligands ( $L^1$  and  $L^2$ ) and their complexes are listed in Table 2. The most characteristic vibrations are selected by comparing the IR spectra of the ligands with those of their metal complexes. The strong bands at 1608 and 1639 cm<sup>-1</sup> for free ligands are due to the azomethine vibration modes, v(C=N). These bands shift to the higher frequency in the range 1672–1674 cm<sup>-1</sup> for the complexes of  $L^1$  and 1663–1674 cm<sup>-1</sup> for the complexes of  $L^2$  on complexation through two azomethine nitrogens to metal atom [29]. The upward shifts for the complexes were previously found for the Schiff base complexes [30]. Ligands display a sharp doublets



Fig. 4. Proposed fragments of [Zn<sub>2</sub>L<sup>1</sup>(ClO<sub>4</sub>)<sub>4</sub>].

at 1239–1208 for  $L^1$  and 1234–1211 cm<sup>-1</sup> for  $L^2$  which are assigned to etheric C—O vibration modes. These bands shift to higher/lower frequency in the range 1239–1232 for the complexes of  $L^1$  and 1239–1206 cm<sup>-1</sup> for the complexes of  $L^2$  by the coordination through the two etheric oxygens to metal atom. The perchlorate salts (**3–6**, **8** and **9**) of the complexes show a triplet ( $v_3$  mode) or a broad band at about 1100 cm<sup>-1</sup> (Table 2) due to antisymmetric stretch, which is indicative of the weakly coordinated/uncoordinated perchlorate ion. The lower energy band at about 625 cm<sup>-1</sup> indicates the presence of the coordinated perchlorate ions [31]. In the complexes of **10** and **11**, the broad band 1086 cm<sup>-1</sup> and 1089, 1105, 1147 cm<sup>-1</sup> assigned to  $v_3$ (Cl—O) indicates both coordinated and noncoordinated (ionic) nature of the ClO<sub>4</sub><sup>-</sup> ion, respectively. The ionic nature is further supported by the appearance of a sharp band at 624 and 625 cm<sup>-1</sup>, respectively [32].

The band assignment to various M—N and M—O stretching vibrations in the lower region of the spectra are difficult as the ligand vibration interfere. Hence the assignments made here tentative. In the light of previous results [33], we assign the bands in the region 501–520 and 567–574 cm<sup>-1</sup>, to v(M-N) and v(M-O) stretching vibrations, respectively. They were observed as weak bands indicative of the formation of the metal complexes.

#### 3.3. Molar conductivity

Table 5

The molar conductivity  $(\Lambda_m)$  data, measured at 25 °C using  $10^{-3}$  M solutions of the complexes in DMF (Table 1), showed the presence of ionic and coordinated counterions, since they are in the range reported in that solvent for 2:1 and non-electrolytes

Electronic absorption spectral data with assignments of Schiff base and its complexes.

for the perchlorate complexes, respectively [34]. It seems that two perchlorate ions remain in the inner coordination sphere in the complexes of **10**, **11** while in the complexes of **3–6**, **8**, and **9** all the perchlorate ions are coordinated to the metal ions in solution. This is in agreement with the results obtained from the IR studies.

#### 3.4. Mass spectra

Analysis by ESI mass spectral data indicated ions at m/z 1065.41 (3.8%) [M]<sup>+</sup>, m/z 990.46 (6.3%) [M-phenyl+2]<sup>+</sup> and strong parent ions at m/z 104.97 (100%)  $[C_6H_5HC=N]^+$  for  $L^1$ , at m/z 817.42 (14.6%) [M]<sup>+</sup>, m/z 818.36 (8.9%) [M+1]<sup>+</sup>, m/z 632.40 (5%) [M-(O-C<sub>10</sub>H<sub>6</sub>HC=N-CH<sub>3</sub>)]<sup>+</sup> and strong parent ions at m/z 153.07 (100%)  $[C_{10}H_6HC=N]^+$  for  $L^2$ . Analysis by ESI mass spectral data of  $L^1$  complexes indicated ions at m/z 1572.26 (%41.1) [M]<sup>+</sup> for **3**, m/z 1582.50 (%15.19) [M+2]<sup>+</sup> for **4**, m/z 1590.14 (%3.16) M<sup>+</sup>, for **5**, and m/z 1596.14 (%5.28) M<sup>+</sup>, for **6** (Fig. 3). For the complexes of  $L^2$ , at m/z 1324.68 (%7.1) [M]<sup>+</sup> for **8**, at m/z 1334.18 (%9.4) [M + 2]<sup>+</sup> for **9**, at m/z 1179.4 (%5.5) [M + 2H<sub>2</sub>O-2ClO<sub>4</sub> + 1]<sup>+</sup> for **10**, at m/z 1146.5 (<%1) [M-2ClO<sub>4</sub>+one]<sup>+</sup> for **11** were observed. The schematic fragmentation of the  $[Zn_2L^1(ClO_4)_4]$  is depicted in Fig. 4. All these mass spectral data support the formation of the Schiff bases and their binuclear transition metal complexes.

# 3.5. Electronic spectra and magnetic moments

The electronic spectrum of  $L^1$  and  $L^2$  in DMF shows absorption bands 275 ( $\varepsilon = 28706 \text{ M}^{-1} \text{ cm}^{-1}$ ), 321 nm ( $\varepsilon = 29907 \text{ M}^{-1} \text{ cm}^{-1}$ ),

 $\lambda_{max}$ , nm ( $\sim M^{-1}$  cm<sup>-1</sup>) in DMF Compound Band assignments Geometry L<sup>1</sup>, (**2**) 376 (25492)  $n \rightarrow \pi^*$ 358 (30328), 321 (29907), 275 (28706)  $\pi \to \pi^*$  ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}({}^{4}G)$  ${}^{6}A_{1g} \rightarrow {}^{4}T_{2g}({}^{4}G)$  $[Mn_2L^1(ClO_4)_4], (3)$ Octahedral 977 (14), 462 (1645) LMCT 413 (1904) 360 (2300), 316 (2210), 292 (2056)  $\pi \rightarrow \pi^*$  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}(F)$ 982 (3),  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$ Octahedral  $[Ni_2L^1(ClO_4)_4], (4)$ 471 (167) 411 (1983) LMCT 358 (2411), 312 (2314), 242 (147)  $\pi \to \pi^*$  ${}^{2}E_{g} \rightarrow {}^{2}T_{2g}$ 512 (4112)  $[Cu_2L^1(ClO_4)_4], (5)$ 411 (3704) LMCT Octahedral 352 (4194), 301 (4095), 242 (660)  $\pi \rightarrow \pi^*$  $[Zn_2L^1(ClO_4)_4], (6)$ 405 (2036) LMCT Octahedral 358 (2610), 316 (2573), 251 (197)  $\pi \rightarrow \pi^*$ 379 (2665)  $n \rightarrow \pi^*$  $L^{2}$ , (**7**) 358 (4018), 334 (3790), 321 (3848)  $\pi \to \pi^*$ 310 (3754)  $\label{eq:alpha} \begin{array}{l} {}^{6}A_{1g} \rightarrow {}^{4}T_{1g}({}^{4}G) \\ {}^{6}A_{1g} \rightarrow {}^{2}T_{2g}({}^{4}G) \\ {}^{6}A_{1g} \rightarrow {}^{4}A_{1g}, \, {}^{4}E_{g}({}^{4}G) \end{array}$ 564 (287). 531 (302).  $[Mn_2L^2(ClO_4)_4], (8)$ 500 (307), Octahedral 445 (300). LMCT 410 (288)  $\pi \rightarrow \pi^*$ 352 (36168), 312 (40370), 272 (28004) 981 (3)  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}(F)$  $^{3}A_{2g}(F) \rightarrow ^{3}T_{1g}(F)$ 465 (162)  $[Ni_2L^2(ClO_4)_4], (9)$ 403 (289) LMCT Octahedral 358 (32444),330 (40595), 312 (4000),  $\pi \rightarrow \pi^*$ 271 (24443), 241 (3560) 596 (282)  $z^2 \rightarrow x^2 - y^2$  $[Cu_2L^2(ClO_4)_2](ClO_4)_2$ , (10) 490 (870) LMCT Square pyramidal 411 (361)  $\pi \rightarrow \pi^*$ 358 (37729), 334 (36819), 274 (30854245 (4540) 463 (3261), LMCT  $[Zn_2L^2(ClO_4)_2](ClO_4)_2, (11)$ Square pyramidal 411 (3222)  $\pi \rightarrow \pi^*$ 349 (29611), 322 (30265), 272 (23312) 242 (3640)

358 nm ( $\varepsilon$  = 30328 M<sup>-1</sup> cm<sup>-1</sup>), 376 nm ( $\varepsilon$  = 25492 M<sup>-1</sup> cm<sup>-1</sup>) and 310 ( $\varepsilon$  = 3754 M<sup>-1</sup> cm<sup>-1</sup>), 321 ( $\varepsilon$  = 3848 M<sup>-1</sup> cm<sup>-1</sup>), 334 ( $\varepsilon$  = 3790 M<sup>-1</sup> cm<sup>-1</sup>), 358 ( $\varepsilon$  = 4018 M<sup>-1</sup> cm<sup>-1</sup>), 379 ( $\varepsilon$  = 2665 M<sup>-1</sup> cm<sup>-1</sup>), respectively. The bands appearing at the low energy side are attributable to  $n \rightarrow \pi^*$  transitions associated with the azomethine chromophores. The bands at higher energy arise from  $\pi \rightarrow \pi^*$ transitions within the phenyl and naphthyl rings [35]. The absorption bands of the complexes are shifted to longer wavelength region compared to those of the ligand [36]. A moderate intensive band observed in the range of 405–413 and 403–490 nm is attributable to the LMCT transitions of  $L^1$  and  $L^2$  complexes, respectively. This shift may be attributed to the donation of the lone pairs of electron of the nitrogen atoms of the Schiff base to the metal ion ( $M \leftarrow N$ ).

The electronic spectra of the binuclear Cu(II) complexes are recorded in DMF solution. The electronic spectrum shows a single absorption bands at 19531 cm<sup>-1</sup> (512 nm) for **5**. The positions of the band are of typical d–d transitions in the octahedral Cu(II) surrounding [37,38]. The absorption spectrum of **10** shows a broad peak centered at 16779 cm<sup>-1</sup> (596 nm) due to  $z^2 \rightarrow x^2 - y^2$  transition and that of Cu(II) exhibits square pyramidal geometry [37,39–42]. The  $\mu_{\text{eff}}$  values (1.88 and 1.90 BM) support ferromagnetic type interactions in the Cu(II) complexes and these are consistent with the proposed geometries.

The electronic spectra of the dinuclear Mn(II) complexes exhibit two absorption bands at 21,645 (462 nm) and 10,235 cm<sup>-1</sup>(977 nm) for **3**, three absorption bands at 20,000 cm<sup>-1</sup> (500 nm) and 18,832 cm<sup>-1</sup>(531 nm), 17,730 cm<sup>-1</sup>(564 nm) for **8** suggesting an octahedral geometry. The band assignments were given in Table 5 and the  ${}^{6}A_{1g} \rightarrow {}^{4}A_{1g}$ ,  ${}^{4}E_{g}({}^{4}G)(\nu_{1})$  transition for complex **3** is thought to be hindered by very intense and broad  $\pi \rightarrow \pi^{*}$  and  $n \rightarrow \pi^{*}$  transitions. For the complex **3** and **8**, the observed magnetic susceptibility value of 5.27 and 3.79 BM is in accordance with the high spin six coordinated octahedral arrangement around manganese complex [38,43]. The low moment of **8** may be ascribed to superexchange takes place between manganese(II) ions.

Typical octahedral Ni(II) complex is expected to exhibit three bands which are assignable to  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$ ,  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$ and  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}(F)$  transitions. The Ni(II) complexes in this study exhibits only two absorptions bands at 21,231 (471 nm) and 10,183 cm<sup>-1</sup> (982 nm) for **4**, 21,505 (465 nm) and 10,194 cm<sup>-1</sup> (981 nm) for **9** and assignable to  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$  and  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}(F)$  transitions for the two complex, respectively. The  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$  transition was hindered by the intense  $n \rightarrow \pi^{*}$  transitions. From these transitions and magnetic moment values (2.45 and 2.96 BM) a high spin octahedral geometry is assigned for **4** and **9** [44].

UV/visible spectra of the binuclear Zn(II) complexes (**6** and **11**) were recorded in DMF solution showed two main peaks at 405, 358–241 and 411, 358–245 nm, respectively. These peaks were assigned to Zn-L charge-transfer transition as well as intra ligand transition, respectively.

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# Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2009.01.037.

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