



## Synthesis and characterisation of Mononuclear and Tetranuclear Zinc(II) Complexes of Schiff Bases Derived from Phenylenediamine

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### ABSTRACT

A mononuclear and new tetranuclear metal complexes of Zn(II) with Schiff base ligands L1 and L2 respectively, were synthesised. L1 was obtained through the condensation of salicylaldehyde with *ortho*-phenylenediamine while L2 was the product of reaction between of *ortho*-vanillin with 2,4,6-trimethyl-*m*-phenylenediamine. The ligands and complexes were characterised via elemental analysis, melting point, IR and NMR spectroscopy. The shifting of  $\nu(\text{C}=\text{N})$ ,  $\nu(\text{C}-\text{OH})$  and  $\nu(\text{O}-\text{CH}_3)$  infrared peaks upon coordination with Zn(II) indicated that these three moieties play a significant role in the complexation. It was found that L1 acted as tetradentate ligand, coordinating with Zn(II) centres through phenolic oxygen and imine nitrogen. The ligand L2 acted as a hexadentate ligand, bonded to metal via phenolic oxygen, imine nitrogen and methoxy oxygen, where four Zn(II) centres formed bridges to connect two ligands.

*Keywords:* Schiff base, metal complexes, mononuclear, tetranuclear

### INTRODUCTION

The condensation reaction of primary amines with active carbonyl compounds results in the formation of Schiff base compounds and this was reported by Hugo Schiff in 1864 (Qin et al., 2013). Schiff bases have the general formula of  $\text{RR}'\text{C}=\text{NR}''$  containing  $\text{C}=\text{N}$  functional group. Structurally, a Schiff base is a nitrogen analogue of an aldehyde or ketone in which the carbonyl group ( $\text{C}=\text{O}$ ) is replaced by an imine or azomethine group (Abu-Dief et al., 2015). The formation of a Schiff base involves two steps: a nucleophilic addition of primary

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amine followed by formation of a carbinolamine intermediate (Cordes & Jencks, 1963) before elimination of a water molecule.

Schiff bases can be effective chelating agents acting as mono-, di- or polydentate ligands depending on the number of donor atoms present in the molecule and can form generally five or six-membered chelate rings upon reaction with a metal ion (Alim et al., 2015). Schiff bases with sulphur and nitrogen donor atoms in their structures act as good chelating agents for transition and non-transition metal ions. Coordination compounds to metal ions, such as copper, nickel, zinc, cadmium and cobalt, have been reported to enhance their biological activities (El-Sonbati et al., 2016).

## METHOD

### Materials

All the chemicals and solvents used were of analytical grade. Salicylaldehyde (Sal), ortho-vanillin (Ovan), 2,4,6-trimethyl-m-phenylenediamine (3CH<sub>3</sub>-MPD), ortho-phenylenediamine (OPD), zinc(II) acetate dihydrate, methanol, ethanol, chloroform, deuterated chloroform and dimethylsulfoxide (DMSO) were purchased from Sigma Aldrich and used without further purification.

### Synthesis of Ligands and Metal Complexes

**Synthesis of L1.** Sal was mixed with OPD in 2:1 ratio in absolute ethanol. The mixture was refluxed and stirred under N<sub>2</sub> for an hour. The orange precipitate formed was filtered off, rinsed with cold methanol and dried in-vacuo over blue silica gel, yielding 93.0%. The reaction scheme is shown in Figure 1.

**Synthesis of L2.** 3CH<sub>3</sub>-MPD and Ovan were mixed in absolute ethanol in 2:1 ratio. The mixture was refluxed and stirred under N<sub>2</sub> for an hour. The orange precipitate formed was filtered off, rinsed with cold methanol and dried under vacuum over blue silica gel, yielding 88.6%. The reaction scheme is shown in Figure 2.

**Synthesis of ZnL1.** L1 and zinc(II) acetate dihydrate were mixed in 1:1 ratio in ethanol and refluxed with stirring for an hour. The yellowish precipitate formed was filtered off, rinsed with cold ethanol and dried in desiccator over blue silica gel, yielding 97.0%.

**Synthesis of Zn<sub>4</sub>L2.** Synthesis of Zn<sub>4</sub>L2 was carried out via a microwave method where L2, zinc(II) acetate dihydrate, triethylamine and absolute EtOH were mixed in a microwave reaction capsule, heated at 160°C for 15 minutes in a microwave at 1000 rpm. A yellow precipitate was observed and the reaction mixture was chilled overnight. The solid was filtered off, rinsed with cold ethanol and dried in a desiccator over blue silica gel, yielding 50.4%.

## Physical measurement

The elemental analyses of the synthesised compounds were carried out using Flash EA 110 Elemental Analyzer. IR spectra were recorded as KBr discs using Perkin Elmer FT-IR 1600 Spectrometer from 450  $\text{cm}^{-1}$  to 4000  $\text{cm}^{-1}$ . The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  and deuterated DMSO using Bruker Avance 300 MHz spectrometer. The melting points of the compounds were recorded using Stuart Melting Point SMP10.

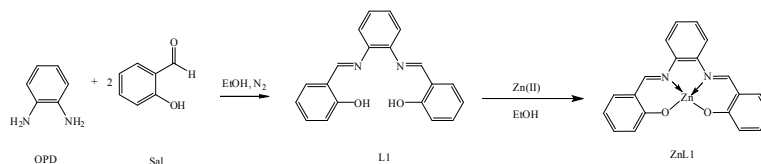


Figure 1. Reaction scheme for synthesis of L1 and ZnL1

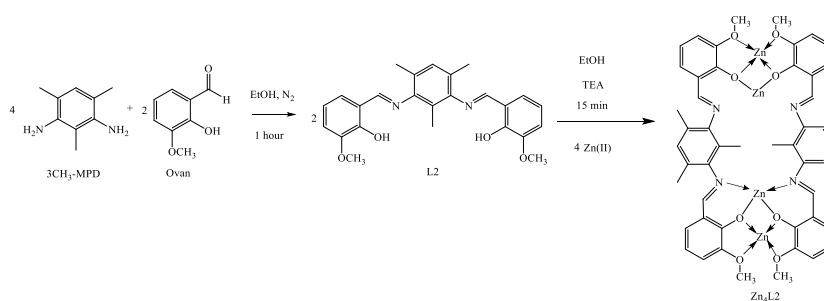


Figure 2. Reaction scheme for synthesis of L2 and  $\text{Zn}_4\text{L}_2$

## RESULTS AND DISCUSSION

Table 1 displays the physical properties and results of elemental analysis of the compounds. The melting points of the organic ligands were much lower than those of the metal complexes, as expected, mostly due to the larger molecular sizes of the complexes and presence of stronger dative covalent bond and ionic bond. The experimental and calculated C, H and N percentages were in close accord, indicating that the expected compounds have been obtained.

Table 1  
*Physico-chemical data of L1, L2, Zn(L1) and Zn<sub>4</sub>(L2)<sub>2</sub>*

Compound	Molecular Formula (RMM)	Melting Point (°C)	Elemental Percentages Found (Calculated)		
			C (%)	H (%)	N (%)
L1	C <sub>20</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub>	170	75.07	5.10	8.32
Zn(L1)	(316.36)		(75.93)	(5.00)	(8.86)
	C <sub>20</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> Zn(CH <sub>3</sub> CO <sub>2</sub> )	> 300	59.29	4.03	8.11
(CH <sub>3</sub> CO <sub>2</sub> )	(438.72)		(60.22)	(3.91)	(6.38)
L2	C <sub>25</sub> H <sub>26</sub> N <sub>2</sub> O <sub>4</sub>	151	71.74	6.38	6.57
	(418.49)		(71.75)	(6.26)	(6.69)
Zn <sub>4</sub> (L2) <sub>2</sub>	C <sub>50</sub> H <sub>48</sub> N <sub>4</sub> O <sub>8</sub> Zn <sub>4</sub>	> 300	53.60	4.44	4.35
	(1094.47)		(54.87)	(4.42)	(5.12)

### Infrared Spectroscopy

The relevant infrared data are tabulated in Table 2. The spectra of L1 (Figure 3) and L2 (Figure 4) exhibit a peak around 3200 cm<sup>-1</sup> due to the O-H stretching vibrations in concordance with the report by Fugu et al. (2013) and this peaks are absent in the ZnL1 and Zn<sub>4</sub>L2 spectra, indicating deprotonation of phenolic oxygen upon coordination with zinc(II). This was corroborated by the shifting to lower frequencies of the ν(C-O) (phenolic) in both ZnL1 and Zn<sub>4</sub>L2 when compared with the parent ligands L1 and L2 respectively, indicating direct involvement of phenolic O in complexation.

The strong sharp peaks at 1612 and 1617 cm<sup>-1</sup> in L1 and L2 respectively, are attributed to the ν(C=N) as reported by Bahron et al. (2012) and Abdel-Kader et al. (2016). These peaks shifted in ZnL1 and Zn<sub>4</sub>L2 spectra indicating that the imine nitrogen is involved in the coordination with Zn(II), where the lone pair of electrons on N is shared with the Zn centre in a dative manner.

Arshad et al. (2016) reported that the ν(M-N) and ν(M-O) peaks would appear in the region below 600 cm<sup>-1</sup>. New weak bands at 550 cm<sup>-1</sup> and 560 cm<sup>-1</sup> in the spectra of ZnL1 and Zn<sub>4</sub>L2 respectively, are attributable to ν(M-N). The peaks for ν(M-O) were not detected, and expected to be below 500 cm<sup>-1</sup>. The ν(C-O) of the methoxy group in Zn<sub>4</sub>L2 is observed in a lower frequency than in the parent ligand L2, signifying the involvement of methoxy oxygen in bonding with Zn to form the tetranuclear complex. This data supports the suggested structure of Zn<sub>4</sub>L2 in Figure 2.

L1 is indicated to act as a tetradentate chelating agent as it bonds to metal ion via two phenolic oxygens and two azomethine nitrogen. On the other hand, L2 acts as a hexadentate ligand, coordination to zinc(II) centres via two methoxy O, two phenoxo O and two imino N donor atoms.

Table 2  
Infrared data of L1, L2, Zn(L1) and Zn<sub>4</sub>L2

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{O})$ Phenolic	$\nu(\text{C}-\text{O})$ Methoxy	$\nu(\text{M}-\text{N})$
L1	1612	1276	-	-
ZnL1(CH <sub>3</sub> CO <sub>2</sub> )	1615	1179	-	550
L2	1617	1255	1088	-
Zn <sub>4</sub> L2	1607	1219	1076	560

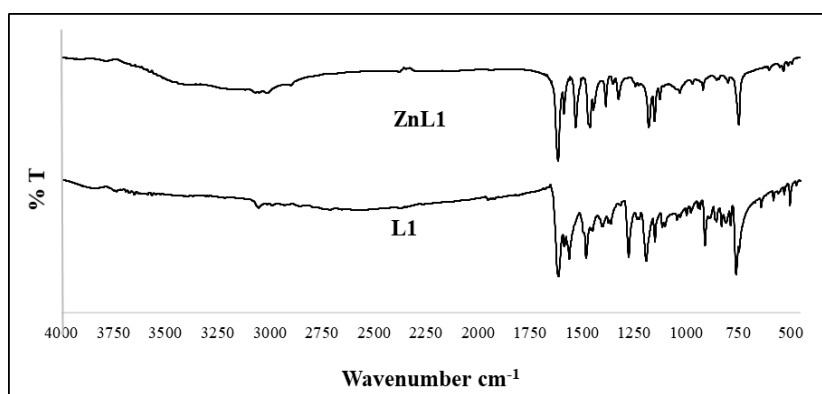


Figure 3. The IR spectra of L1 and ZnL1

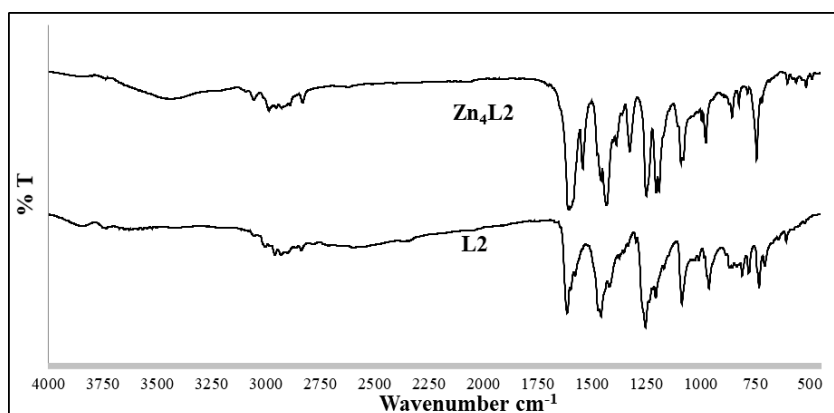


Figure 4. The IR spectra of L2 and Zn<sub>4</sub>L2

### <sup>1</sup>H NMR Spectroscopy

<sup>1</sup>H NMR data provided additional support and significant evidence regarding the formation of complexes. The spectrum of L1 (Figure 5) shows signals at 13.12, 9.92 and 6.87-7.53 ppm corresponding to phenolic, azomethine and aromatic protons respectively. The O-H signal in

L1 appears around 13.0 ppm, heavily shielded due to the presence of O and possible inter- or intramolecular hydrogen bonding. The absence of O-H peak in ZnL1 spectrum indicated the deprotonation of OH upon coordination with zinc(II) through the phenolic oxygen.

The imine proton signal shifted slightly upfield in ZnL1 complex indicating that the imine nitrogen is involved in coordination with the metal ion. Similar observation was made in <sup>1</sup>H NMR spectra of L2 and Zn<sub>4</sub>L2 (Figure 6). The OH signal at 9.95 ppm disappeared in Zn<sub>4</sub>L2 indicating deprotonation upon complexation. The singlet at 8.30-8.37 attributed the signal of azomethine proton of L1. This peak shows an upfield shift in Zn<sub>4</sub>L2 complex. The methoxy and methyl chemical shifts of both L2 and Zn<sub>4</sub>L2 appear at regions 3.95-3.89 ppm and 1.60-2.30 ppm respectively.

The chemical shift at 0.85 ppm of ZnL1 assignable to acetate corroborated with elemental analysis data that shows the presence of acetate Najjihah et al.(2010), either as part of the compound or as an impurity.

Table 3  
<sup>1</sup>H NMR data of L1, L2, Zn(L1) and Zn<sub>4</sub>(L2)<sub>2</sub>

Compound	N=C-H	O-H	Ar-H	OCH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub> CO <sub>2</sub>
L1	9.92 (s)	13.12 (s)	6.87-7.53 (m)	-	-	-
ZnL1(CH <sub>3</sub> CO <sub>2</sub> )	8.98 (s)	-	6.47-7.85 (m)	-	-	-
L2	8.30-8.37 (s)	9.95 (s)	6.92-7.29 (m)	3.95-4.10 (s)	2.07-2.30 (s)	-
Zn <sub>4</sub> L2	7.88-8.37 (s)	-	6.56-7.21 (m)	3.89-3.98 (s)	1.60-2.35 (s)	0.85 (s)

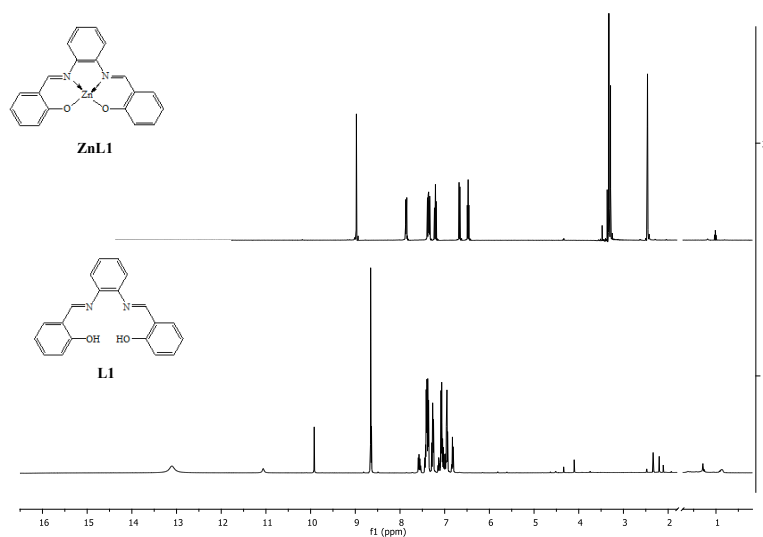


Figure 5. <sup>1</sup>H NMR spectra of L1 and ZnL1

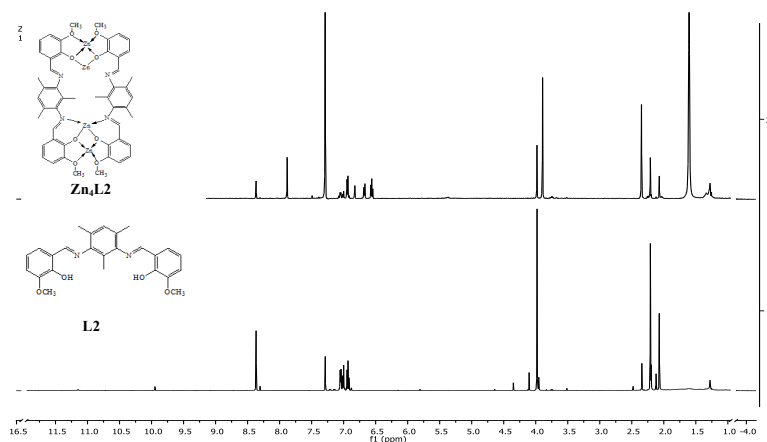


Figure 6.  $^1\text{H}$  NMR spectra of L2 and  $\text{Zn}_4\text{L}_2$

## CONCLUSION

A mononuclear and new tetranuclear zinc complexes were synthesised by complexation of phenylenediamine Schiff base ligands L1 and L2 with zinc(II). All compounds were successfully characterised using elemental analysis, melting point,  $^1\text{H}$  NMR and IR spectroscopy.

## ACKNOWLEDGEMENT

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