Microwave Assisted Synthesis and Characterisation of Trinuclear Zinc(II) Schiff Base Complexes Derived from *m*-phenylenediamine and Salicylaldehyde

Karimah Kassim[1], **Muhamad Azwan Hamali**[2]

[1]Institute of Science, Universiti Teknologi MARA,
40450 Shah Alam, Selangor, Malaysia
[2] Faculty of Applied Sciences, Universiti Teknologi MARA,
40450 Shah Alam, Selangor, Malaysia
E-mail: [1]karimah@salam.uitm.edu.my,
[2]azwan_hamali@yahoo.com

Accepted: 31 May 2017
Received: 26 January 2017

ABSTRACT

A series of Schiff base ligand, SALMPD, and its mono- and trinuclear Zn(II) metal complexes were synthesised from m-phenylenediamine and salicylaldehyde in alcoholic solution. The synthesis of ligand and mononuclear complex were synthesised using conventional condensation method, while the trinuclear complex was done using microwave-assisted synthesis method. The structure of each compound was elucidated by elemental analysis, infrared and ^1H NMR spectroscopy. The infrared spectrum of SALMPD shows a strong azomethine (C=N) band at 1621.62cm^{-1}, indicates the formation of the ligand. Upon complexation of the mononuclear complex, the C=N infrared band shifted and the disappearing of the phenolic hydrogen signal in ^1H NMR suggesting the chelation between Zinc(II) metal ion and ligand took place when azomethine and phenolic hydrogen deprotonated. The trinuclear complex, Zn_3(SALMPD) obtained was consist of two moieties of mononuclear Zn(SALMPD), which act as ligands that chelating to the third Zn(II) metal ion through oxygen atom due to the shifting of M-O infrared band from 575.12-540.53cm^{-1}, which serves as a coordination site for the metal ion.

Keywords: *schiff base, m-phenylenediamine, salicylaldehyde, zinc, multinuclear*

INTRODUCTION

Many studies on Schiff bases has been conducted extensively which considered to be a ‘privileged ligands’ due to its stability and well-designed structures, as well as their ease in synthesising [1]. Ligands consisting of nitrogen (N), oxygen (O) or sulphur (S) donor atom are found to be biologically actives. This contributes to a wide range of biological application such as antimicrobial [2], anticancer [3] and antifungal [4]. On top of that, these ligands coordinate with almost all metal ions, capable of stabilising metals in various oxidation states to form complexes [5].

Metal ions are able to coordinate to an aromatic diamine based ligand on their relative *ortho*, *meta* or *para* position directly [6]. This is due to the presence of O, N, N, O tetradentate donor atom which positioned at the two axial open site, providing four coordination site for the metal to provide support to the ligand [7].

Multinuclear complexes have attracted particular interest due to its capability to coordinate more than one metal ion. This feature is biologically important because the complexes synthetically resemble ranges of metalloprotein. Their usage in the biological modeling of the metal active sites of the metalloprotein picks the interest of modern chemist to synthesis and characterisation of polynuclear complexes [8-9]. In order to prepare multinuclear complexes, a simple metal ion complex is firstly synthesised. This simple ion complex will serve as ligands for another metal ion [10].

The conventional method of synthesising multinuclear complexes is time-consuming and thus, replacing the conventional method with microwave assisted synthesis could overcome this problem. Microwave assisted synthesis has been developed and been explored broadly by the researcher. The irradiation that comes from the microwave not only shorten the reaction time, it also increased yield and eco-friendly, due to minimum usage of solvent [11-12].

In this paper, mono- and trinuclear zinc(II) complex were synthesised from Schiff base ligand derived from *m*-phenylenediamine and salicylaldehyde. The structures were elucidated using elemental analyses, FTIR and NMR.

MATERIALS AND METHOD

Chemicals and Materials

M-phenylenediamine (MPD), salicylaldehyde, zinc(II) acetate dihydrate, and triethylamine used in this research were purchased from Sigma Aldrich, while the solvent such as methanol and ethanol were analytical reagent grade purchased from Merck. All chemicals were used without further purification.

Instrumental

To synthesise the proposed trinuclear Zn(II) complex, Anton Paar Monowave 400 microwave was used. Elemental analyses were conducted on Flash EA 110 Elemental Analyzer. Infrared spectra were recorded using in the wavelength region of 4000-450cm^{-1} using Perkin Elmer 1600 Spectrometer. The proton NMR spectra for ligand solution and complexes dissolved in D_6-DMSO and $CDCL_3$ respectively were obtained using Bruker Avance 300 MHz. The melting point of the ligand and complexes were determined in a one-end capillary tube using BÜCHI Melting Point B-545 apparatus.

Synthesis

The overall reaction for the syntheses Schiff base and its mono- and trinuclear zinc complexes is represented in Figure 1.

Synthesis of Ligand, SALMPD

The Schiff base ligands were prepared according to the published literature method [13]. *M*-phenylenediamine (5mmol, 0.54g) dissolved in 15mL MeOH was added dropwise to (10mmol, 1.22g) salicylaldehyde in 15mL MeOH solution. The mixture was refluxed for three hours with continuous stirring. The yellow precipitate was filtered off and washed with cold MeOH. The obtained ligand was then recrystallised using EtOH and dried in a vacuum desiccator.

Synthesis of Mononuclear Complex, Zn(SALMPD)

The synthesised SALMPD ligand (3mmol, 0.94g) was dissolved in EtOH, to which was added with equimolar ethanolic solution of $Zn(CH_3COO)_2.2H_2O$. The mixture was refluxed for three hours. The resulting yellowish precipitate was filtered and washes with cold EtOH and dried in a vacuum desiccator.

Synthesis of Trinuclear Complex, Zn_3(SALMPD)

The Zn_3(SALMPD) complex was synthesised using the method as described by [14] with slight modification. The previously synthesised mononuclear complex (1mmol, 0.37g) was mixed equimolar with $Zn(CH_3COO)_2.2H_2O$ in 5mL EtOH with the addition drops of triethylamine. The microwave condition was set at speed of a 1000rpm and heat up to 160^{o}C. The reaction took place for 15 minutes before the yellow precipitates were filtered and rinsed with cold ethanol. The product was dried in a vacuum desiccator.

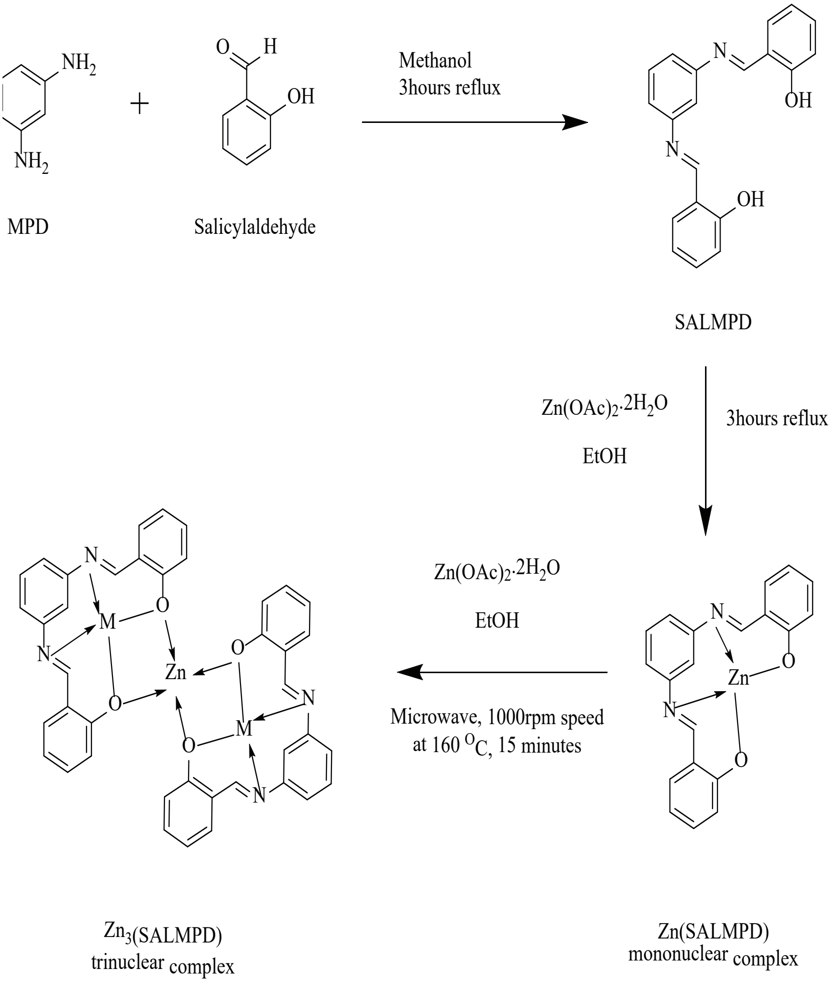

Figure 1: The synthesis routes of SALMPD, Zn(SALMPD) and Zn_3(SALMPD)

RESULT AND DISCUSSION

Synthesis of Schiff Bases

SALMPD ligand was prepared through condensation of *m*-phenylenediamine and salicylaldehyde in EtOH, with the ratio of 2:1. The ligand, which is the precursor for the formation of mononuclear zinc complex, was checked using elemental analysis and the physical properties are shown in Table 1.

The elemental analysis of the ligand is confirmed to be similar as previously reported [15]. From Table 1, the corresponding data of Zn(SALMPD) and Zn_3(SALMPD) suggested that these complexes are dimers.

Table 1: Analytical data of the ligand, mono- and trinuclear Zn complex

Comp.	**Emp for. (molc. Mass)**	**Yield (%)**	**Melting point (°C)**	**Elemental analysis Calc. (Found) (%)**		
				C	**H**	**N**
SALMPD	$C_{20}H_{16}N_2O_2$ (316.36)	93.45	110	75.93 (76.09)	5.10 (5.07)	8.86 (9.15)
Zn(SALMPD)	$C_{20}H_{14}N_2O_2Zn$ (379.72)	85.08	>300	63.26 (60.39)	3.72 (3.84)	7.38 (5.07)
Zn_3(SALMPD)	$C_{40}H_{28}N_4O_4Zn_3$ (820.80)	67.25	>300	58.53 (53.35)	2.95 (3.30)	6.83 (6.01)

Infrared Spectroscopy

The important vibrational modes of the functional group for the ligand and its respective complexes are described in Table 2 and Figure 2. A strong absorption band at 1621.62cm^{-1} for ligand SALMPD is assigned to be the azomethine (C=N) functional groups. This band was shifted to a lower frequency in complex Zn(SALMPD) by approximately 20cm^{-1}. The shifting indicates that the coordination between the free ligand and metal ion through azomethine nitrogen was a success [8]. As for the tri-nuclear complex, the C=N absorption band only show small shifting since there are no new atoms coordinates at the azomethine nitrogen.

Another strong band from the ligand was detected at 1275.28cm^{-1}, assigned to be the stretching vibration of the C-O of the phenolic group. Similarly, the band shifted to a lower frequency at 1148.23cm^{-1} indicates the chelation of the metal ion to the ligand through oxygen atom of the phenolic group [16].

The shifting of C=N and C-O vibrational band in Zn(SALMPD) and Zn_3(SALMPD) leads to the formation of a new band in the low the wavelength region. The weak intensity band observed at 609.71cm^{-1} and 607.87cm^{-1} respectively were found to be the M-N bond, while the vibrational band 575.12cm^{-1} from Zn(SALMPD) attributes the present of M-O stretching bond. As for complex Zn_3(SALMPD), the M-O vibrational band was shifted to 540.53cm^{-1}, confirming the coordination of the third metal ion with another two mononuclear complex Zn(SALMPD).

Table 2: Infrared spectral data of ligand, mono- and trinuclear Zn complex

Comp.	**Assignments (cm^{-1})**				
	v(C=N)	**v(C=C)**	**v(C-O)**	**v(M-N)**	**v(M-O)**
SALMPD	1621.62	1459.52	1275.28	-	-
Zn(SALMPD)	1606.43	1439.85	1148.23	609.71	575.12
Zn_3(SALMPD)	1604.95	1440.26	1147.27	607.87	540.53

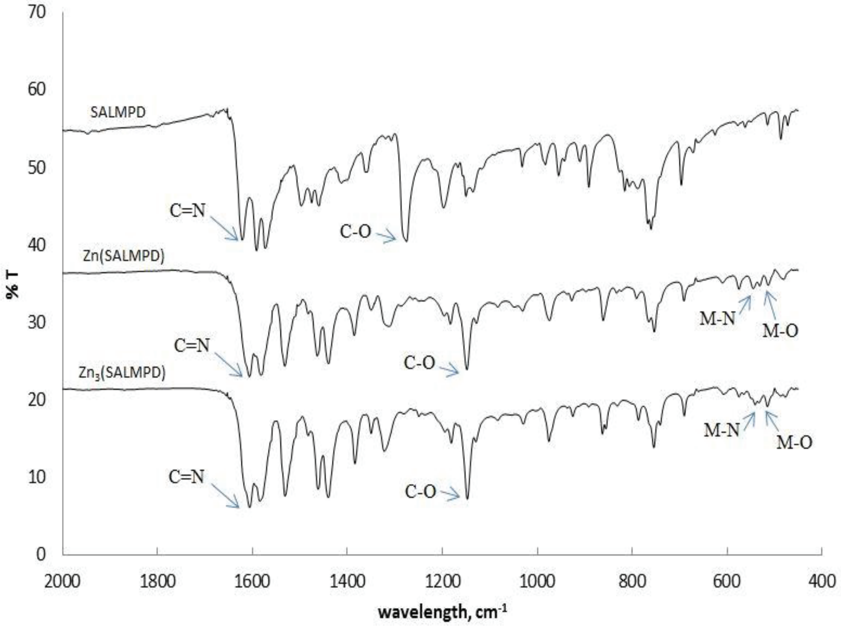

Figure 2: FTIR spectra of free ligand (SALMPD), Zn(SALMPD) complex, Zn_3(SALMPD)

^{1}H NMR Spectroscopy

The ^{1}H NMR spectra of the free ligand, SALMPD and its mono- and trinuclear zinc complex were recorded in D_6-DMSO and $CDCL_3$ respectively and it's chemical shifts are given in Table 3. The spectra of SALMPD ligand showed a single peak on the low field region at 13.14 ppm indicated the presence of phenolic hydroxyl proton. This peak is not visible in the mono- and trinuclear complex, Zn(SALMPD) and Zn_3(SALMPD) suggesting that chelation of the metal ion occurred when the hydroxyl deprotonated. The peak observed at 8.71 ppm in free ligand SALMPD is attributed to azomethine (HC=N) proton and as the shifting of the azomethine chemical shift in Zn(SALMPD) and Zn_3(SALMPD) towards upfield region suggested the complexation between ligand and metal ion.

Table 3: Chemical shifts (ppm) for ^{1}H NMR of ligand, mono- and trinuclear Zn complex

Comp.	Chemical shifts, δ (ppm)		
	O-H	HC=N	Ar. protons
SALMPD	13.14	8.71	7.50-6.98
Zn(SALMPD)	-	8.68	7.50-6.61
Zn_3(SALMPD)	-	8.67	7.44-6.61

CONCLUSION

A series of mono- and trinuclear zinc complexes derived from *m*-phenylenediamine and salicylaldehyde has been successfully synthesised and the structure of these compounds has been elucidated using elemental analysis, melting point, infrared and ^{1}H NMR spectroscopy. More structural data such as magnetic susceptibility, molar conductivity, and thermogravimetric analysis are required to determine the compound's magnetism, geometrical shape, as well as to determine the presence of counter-ion in the complexes. Future work on anticancer activity will be studied in vitro using cell line. Previous studies hypothesised that complexation of Schiff base ligand enhances the biological properties of the free ligand while decreasing the toxicity effect from the metal ion. Other than that, microwave irradiation technique provided a quick, clean, and effective synthesis.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the help of Universiti Teknologi MARA (UiTM) in providing the facilities and the Malaysian Ministry of Higher Education for the research grant fund (600-RMI/FRGS 5/3 (0068/2016).

REFERENCES

[1] R. C. Maurya, H. Singh, A. Pandey, and T. Singh, 2001. Metal Chelates of Bioinorganic and Catalytic Relevance: Synthesis, Magnetic and Spectral Studies of Some Mononuclear snd Binuclear Oxovanadium (Lv) and Dioxotungsten (VI) Complexes Involving Schiff Bases Derived from 4-Butyryl-3- Methyl-L-Phenyl-2-Pyrazolin-5-One and Certain Aromatic Amines, *Indian Journal of Chemistry, Vol. 40*(October), pp. 1053–1063.

[2] O. Taheri, M. Behzad, A. Ghaffari, M. Kubicki, G. Dutkieicz, A. Bezzatpour, H. Nazari, A. Khaleghian, A. Mohammadi, M. Salehi, 2014. Synthesis, Crystal Structures and Antibacterial Studies of Oxidovanadium(IV) Complexes of Salen-Type Schiff Base Ligands Derived from Meso-1, 2-Diphenyl-1, 2-Ethylenediamine, *Transit. Met. Chem., Vol. 39*(2), pp. 253–259. https://doi.org/10.1007/s11243-014-9798-9

[3] M. Damercheli, D. Dayyani, M. Behzad, B. Mehravi, and M. S. Ardestani, 2015. New Salen-Type Manganese(III) Schiff Base Complexes Derived from Meso-1,2-Diphenyl-1, 2-Ethylenediamine: in Vitro Anticancer Activity, Mechanism of Action, and Molecular Docking Studies, *J. Coord. Chem.*, *Vol. 68*(9), pp. 1500–1513. https://doi.org/10.1080/00958972.2015.1027697

[4] M. M. Abo-Aly, A. M. Salem, M. A. Sayed, and A. A. Abdel Aziz, 2015. Spectroscopic and Structural Studies of The Schiff Base 3-Methoxy-N-Salicylidene-O-Amino Phenol Complexes With Some Transition Metal Ions and Their Antibacterial, Antifungal Activities, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc., Vol. 136*(PB), pp. 993–1000. https://doi.org/10.1016/j.saa.2014.09.122

[5] K. C. Gupta and A. K. Sutar, 2008. Catalytic Activities of Schiff Base Transition Metal Complexes, *Coord. Chem. Rev., Vol. 252*(12–14), pp. 1420–1450. https://doi.org/10.1016/j.ccr.2007.09.005

[6] R. Hernandez-Molina, A. Mederos, P. Gili, S. Dominguez, F. Lloret, J. Cano, M. Julve, C. Ruiza Perez, X. Solans, 1997. Dimer Species in Dimethyl Sulfoxide-Water (80:20 W/W) Solution of N,N'-Bis(Salicylideneimine)-M-Phenylenediamine (H2sal-M-Phen) and Similar Schiff Bases With Cuii, Niii, Coii And Znii. Crystal Structure of [Co2(sal-m-phen)2]CHCl3, *J. Chem. Soc., Dalt. Trans.,* (22), pp. 4327–4334. https://doi.org/10.1039/A702151H

[7] P. G. Cozzi, 2014. Metal-Salen Schiff Base Complexes in Catalysis: Practical Aspects, *Chem. Soc. Rev., Vol. 33*(7), pp. 410–421. https://doi.org/10.1039/B307853C

[8] S. N. Abu Bakar, H. Bahron, and K. Kassim, 2010. Synthesis and Characterization of a Novel Schiff Base Derived from 2,4,6-Trimethyl-*M*-Phenylenediamine with O-Vanillin and Its Metal Complexes, CSSR 2010 - *2010 International Conference on Science and Social Research,* pp. 463–466. https://doi.org/10.1109/CSSR.2010.5773821

[9] D. Dey, Kaur, G., Ranjani, A., Gayathri, L., Chakraborty, P., Adhikary, J., Pasan, J., Dhanasekaran, D., R. Choudhury, A., A. Akbarsha, M., Kole, N., Biswas, B., 2014. A Trinuclear Zinc–Schiff Base Complex: Biocatalytic Activity and Cytotoxicity, *Eur. J. Inorg. Chem., Vol. 2014*(21), pp. 3350–3358. https://doi.org/10.1002/ejic.201402158

[10] A. J. Abdulghani and A. M. N. Khaleel, 2013. Preparation and Characterization of Di-, Tri-, and Tetranuclear Schiff Base Complexes Derived from Diamines and 3,4-Dihydroxybenzaldehyde, *Bioinorg. Chem. Appl., Vol. 2013*. https://doi.org/10.1155/2013/219356

[11] M. Chakraborty, S. Baweja, S. Bhagat, and T. Chundawat, 2012. Microwave Assisted Synthesis of Schiff Bases: A Green Approach, *Int. J. Chem. React. Eng., Vol. 10*(1). https://doi.org/10.1515/1542-6580.2973

[12] C. P. Gharu, 2014. Green and Efficient Microwave Assisted Synthesis of Schiff Bases and Hydroxyl Derivatives of 1, 3, 4-Thiadiazole Containing N-Methyl Piperazine Moiety and their Antimicrobial and Antioxidant Potential, *Chem Sci Trans., Vol. 3*(4), pp. 1310–1317. https://doi.org/10.7598/cst2014.904

[13] M. M. El-Ajaily, M. M. Abou-Krisha, A. M. Etorki, F. S. Alassbaly, and A. A. Maihub, 2013. Schiff base derived from phenylenediamine and salicylaldehyde as precursor techniques in coordination chemistry, *J. Chem. Pharm. Res., Vol. 5*(12), pp. 933–938.

[14] N. Karaboecek, S. Karaboecek, and F. Kormali, 2007. Mono-, Di-and Trinuclear Copper (II) Complexes of a Schiff Base Ligand, 2-{(E)-[(6-{[(1E)-(2-hydroxyphenyl) methylene] amino} pyridin-2-yl) imino]-methyl} phenol, *Turkish J. Chem., Vol. 31*(3), pp. 271–277.

[15] M. M. El-Ajaily, M. M. Abou-Krisha, A. M. Etorki, F. S. Alassbaly, and A. A. Maihub, 2013. Schiff base derived from phenylenediamine and salicylaldehyde as precursor techniques in coordination chemistry, *J. Chem. Pharm. Res., Vol. 5*(12), pp. 933–938.

[16] P. Jeslin Kanaga Inba, B. Annaraj, S. Thalamuthu, and M. A. Neelakantan, 2013. Cu(II), Ni(II), and Zn(II) Complexes of Salan-Type Ligand Containing Ester Groups: Synthesis, Characterization, Electrochemical Properties, and In Vitro Biological Activities., *Bioinorg. Chem. Appl., Vol. 2013*. https://doi.org/10.1155/2013/439848