Synthesis and Characterization of Mn(II) Complex Compounds with Ligand Schiff Base 2-methoxy-6((4-methoxyphenylimino)methyl)phenol

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***Abstract*- Mn(II) complex compounds were synthesized from the reaction of $MnCl_2.4H_2O$ with the Schiff base ligand 2-methoxy-6((4-methoxyphenilimino)methyl) phenol, $C_{15}H_{15}NO_3$, by sonication method. The synthesized product has a yield of 83,24%, brownish-red solid, melting point of ~233 ^{0}C. UV-Vis spectrum has optimum absorption at 270, 277, 335, and 615 nm. FT-IR results show absorption bands 533 cm^{-1} and 498 cm^{-1} which indicated M-O and M-N bonds. The ^{1}H-NMR spectrum shows one ligand indicating the presence of 5 signals with 19 protons. Powder X-ray diffraction of the Mn(II) complex shows (intensity 492 (a.u)) at 14^0 diffraction angle was observed**.

Keywords— complex Mn(II); Schiff base; sonication method

I. INTRODUCTION

Schiff base compound is a type of ligand formed from a ketone or aldehyde with a primary amine so that it has an azomethine group RCH=NR'. The presence of the azomethine group provides special features such as selectivity, ease of synthesis, and wide application. In addition, Schiff base compounds have sensitivity to metal ions, especially transition metal ions so that they can bind to form Schiff base complexes [1].

Schiff base complex is one type of complex derived from Schiff base ligands. Schiff base complex compounds form a coordinating covalent bond between the central atom (electron acceptor) and the ligand (electron donor). The coordination covalent bond in complex compounds is due to the presence of an empty orbital on the central atom so that it can be filled by electrons from the ligand. Several studies have tested the activity of the Schiff base complex including antimicrobial activity [2], antibacterial activity [3] as a reaction catalyst [4], and anticancer activity and efficiency in electrochemotherapy [5]. Based on this, it attracted the attention of researchers to develop research in the field of chemistry, especially in Schiff base complex compounds.

Schiff base complexes can be synthesized with several metals. There are good and stable transition metals for use in formation of complexes with basic Schiff ligands, such as Mn(II), Cu(II), Co(II) and Ni(II) metals [6]. Among these transition metals, Mn(II) metal is a transition metal that can act as a central atom. The central atom of Mn has a configuration of [Ar] $3d^5 4s^2$ and there are unpaired electrons in the d orbitals so that it can form a coordinating covalent bond in the product compound. Based on this, Mn metal is an appropriate alternative in the formation of complex compounds as the central atom [13].

Schiff base complex synthesis has been carried out by various methods, including the sonication method [3], reflux method [6], and microwave irradiation [2]. Synthesis using the sonication method has several advantages, namely short reaction time, simple tool operation, and higher synthesis results [7]. Synthesized Schiff base complexes with 4-((E)-((2-((E)-((3-methyl-phenyl)imino)methyl)phenyl) imino)methyl) -N-pentyl-N-(4-((E)-((2-((E)(phenylimino)methyl)phenyl) imino)methyl)phenyl)aniline ligand and metal Cd(II) yielded of 82% using the sonication method [8]. Synthesized a Schiff base complex compound from Zn(II) metal with ligands derived from the reactants triethylenetetramine and cinnamaldehyde using the sonication method yielding a yield of 82% [9].

II. EXPERIMENTAL

A. Physical. measurements.

Melting points product were measured on a Melting Point Apparatus. Electronic spectral data were performed by Shimadzu UV-Visible Varian Cary 50 spectrometer in the range of 200-800 nm. FT-IR spectra were achieved using a Varian Type FT 1000 spectrometer within 4000-400 cm^{-1} range as KBr discs. ^{1}H-NMR spectra were of complex in DMSO-*d6* solution were recorded on a Agilent DD2 500 MHz spectrometer. Powder X-Ray Diffraction (XRD) analysis was performed in range $2\theta = 3 - 90^0$ scanning speed : 10^0/min.

B. Materials

All chemicals used in the investigation were laboratory pure including $MnCl_2.4H_2O$, ethanol (*p.a*) and Schiff base ligand prepared as describe in the earlier reports [14].

C. Synthesis and characterization of mangan(II) complex

$MnCl_2.4H_2O$ 0,989 g (0,5 mmol) and Schiff base 0,257 g, (1 mmol) were dissolved in ethanol (20 mL). The solution was sonicated for 5 minutes at room temperature. The immediate

color change from yellow to brownies-red indicates complexation. [$MnCl_2L(H_2O)_2$]: yield: (83,24%), m.p: >233 ^{0}C. colour: borwnies-red. State: solid.

III. RESULTS

A. *Synthesis*

The complex Schiff base was synthesized by 2-methoxy-6((4-methoxyphenylimino)methyl)phenol with $MnCl_2.4H_2O$ in 1:2 molar ratio in ethanol. The structure of complex give in Scheme 1. The complex well characreized by UV-Visible, FTIR, ^{1}H-NMR and XRD.

B. *UV-Visible*

The UV-Visible spectral data of the compound $MnCl_2.4H_2O$, Schiff base and complex show in Tabel 1.The spectra of ligan has two absorption bands were observed at wavelength of 270-277 nm due to π→π* transition of the aromatic rings and the wavelength of 334 nm due to n→π* transitions of the imine group (C=N).

Table I.
UV-Visible spectral data

Compounds	Wavelength (nm)
$MnCl_2.4H_2O$	213, 262 and 269
Schiff base	270, 277 and 334
Complex	270, 277, 335 and 615

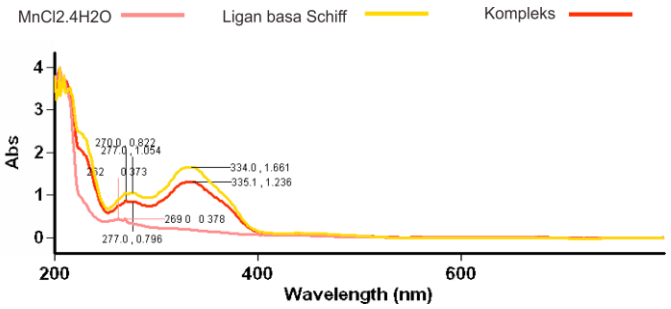

Figure. 1. UV-Vis spectra

The UV-Vis spectra of complex three absorption bands were observed at 270-277 nm due to π→π* transition of the aromatic rings, absorption at 335 nm due to n→π* transitions of the C=N groups. The absorption at 615 nm doe to d→d trasitions of the complex [5]. The UV-Visible spectral of the Schiff base ligand and complex are shown in Figure.1

C. *IR Spectra*

The IR spectrum of the Schiff base ligand and Mn(II) complex are shown in Figure.2. In the Schiff base ligand, the typical functional group vibrates zomethin strain υ(C=N) at wavenumber 1616 cm^{-1}. On complextion, the azomethin group shifted to higher frequency in the 1637 cm^{-1} indicating the coordination of the azomethine nitrogen atom to central metal ion [10]. IR spectral data are given in Table II.

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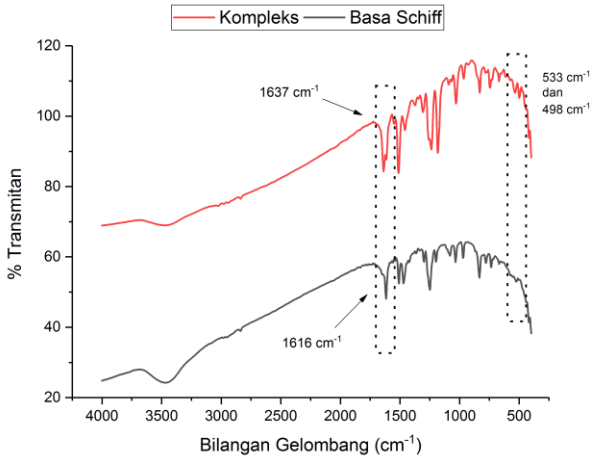
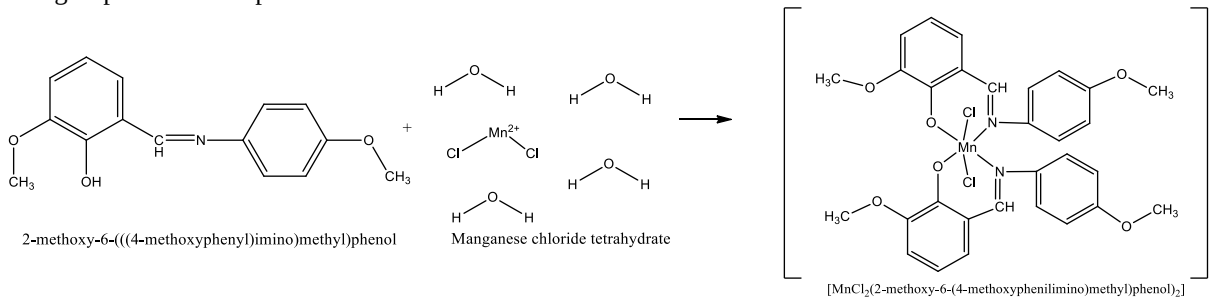


Figure. 2. IR spectra of ligand and complex

The υ(C-O) phenolic band in the complex was shifted from wavenumber 1246 cm^{-1} to lower freguency at wavenumber 1236 cm^{-1} range indicating the coordination of phenolic oxygen atom with the central ion (metal) [11]. The complex spectra shows a wavenumber of 3472 cm^{-1}, which can be attributed to the stretching vibration of the O-H group [10]. The coordinaton of the zomethine nitrogen and phenolic oxygen is further supported by the appearance of two bands at 533 cm^{-1} and 498 cm^{-1} which is assigne to υ(Mn-O) and υ(Mn-N) [5], [6], [10]. From the IR results, it may be concluded that suggested structure show in Scheme 1.



Scheme. 1. Suggested structure for synthesized complex

Table II.
IR spectral data

Functional Group	Wavenumber (cm^{-1})	
	Ligands	Complex
-OH *stretching*	3469	3472
C_{sp2}-H *stretching*	3028	3030
C_{sp3}-H asymetric	2944	2958
C_{sp3}-H symetryc	2835	2837
C=N	1616	1637
C=C aromatic	1508 – 1471	1511 – 1457
C-O-C asymetryc	1297 – 1033	1307
C-O *stretching* phenolic	1246	1236
-CH *bending* aromatic	832	830
Mn-O	-	533
Mn-N	-	498

D. *^{1}HNMR*

The phenolic OH signal of ligand and complex was observed in the offset refion at 13,88 ppm and 13,42 ppm as a broad singlet. The proton phenolic of Schiff base ligand in complex was not deprotonated [12]. The caracterisctic singlet peak at 8,87 ppm futher confirm the azomethine (HC=N) condensation. The aromatic were detected 7,15 (1H, d), 6,84 (1H, t), 7,04 ppm (1H, s), 7,36 ppm (2H, d) and 6,96 (2H, d) respectively. The metoxy –OCH_3 protons were observed as a widening singlet at 3,74 ppm. The complex Mn(II) is paramagnetic. Paramagnetic effect on signal widening, usually can affect one signal or the whole signal. For results proton NMR, it may be concluded that suggested structure show in Scheme 1.

E. P-XRD

Figure 3. shows the P-XRD phase behavior of the $MnCl_2.4H_2O$, Schiff base ligand and complex. The peaks of $MnCl_2.4H_2O$ are given in following: 12, 16, 21 and 29. The peaks of Schiff base ligand are given in following: 12, 19, 21, 23, and 30. The peaks of complex are given in following: 11, 14, 19, 23, and 28. However, in the complex a new peak appeared at 14.

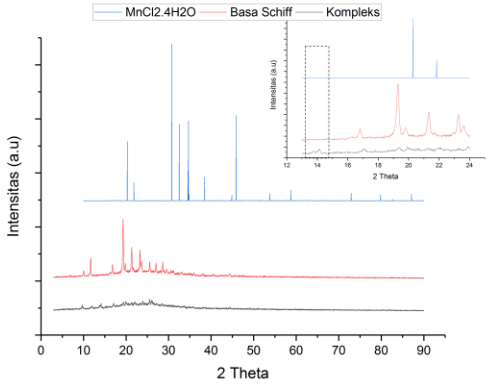


Figure. 4. XRD spectra for $MnCl_2.4H_2O$, ligand and complex

We produced the complex fot the first time, so not avaliable in the literature [5]. The measurement proves that the complex has a polycrystralline phase [5], [10]. For results XRD, it may be concluded that suggested structure show in Scheme 1.

IV. CONCLUSION

Mn(II) form complex of composition $[MnCl_2L(H_2O)_2]$, where L is the Schiff base ligand.. Geometric structure of newly synthesized Mn(II) complex were determined based on the results of UV-Visible, FT-IR, ^{1}HNMR and P-XRD. All spectroscopic data can supports the formation an octahedral structure to the Mn(II) complex (Scheme 1.).

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