INTRODUCTION

The field of Schiff base complexes attracts interest mainly due to facile synthesis and biological activity [1–4]. The diverse structures for the ligands rest with the types of aldehydes and amines [5]. Although obtained ligands involve in a broad scope such as single, double, asymmetric and macrocyclic Schiff bases, etc., the biological activity study of rimantadine-salicylaldehyde (or substituted salicylaldehyde) Schiff bases and their corresponding complexes has not been reported in detail [6].

The clinic medical research indicated that both amantadine (Symmetrel™) and rimantadine (Flumadine™) could block the ion channel formed by the M2 protein of influenza A viruses, result in inhibiting the early stages of virus replication. Therefore in many countries, amantadine and rimantadine have been widely used to treat or prevent seasonal influenza as efficacious remedies [7–10]. However, the incidence of side effects to central-nervous-system was higher with amantadine [11]. Salicylaldehyde and its derivatives are with antibacterial and antiviral activity and they were used to produce efficient herbicides, insecticides and fungicides [12]. Zinc is a vital element in the life for its taking part in a particular metabolic process [13, 14]. The Zn(II) complexes with Schiff bases were also found to be with biological activity and they demonstrated enhanced activities as compared to their parental ligands [15, 16]. In view of these points above, we designed and managed to synthesize a series of complexes containing both metal zinc(II) ion, two corresponding Schiff base ligands and two chlorine atoms; the central zinc atom lies on a twofold rotation axis and is four-coordinate via two chlorine atoms and two oxygen atoms from the Schiff base ligands, forming a distorted tetrahedral geometry.

EXPERIMENTAL

Materials and methods. All chemicals and solvents were of analytical grade and used as received. Elemental analysis was carried out on PerkinElmer Flash EA 1112.
Chemical shifts (δ) for 1H NMR spectra were recorded at 300 MHz on a Varian Mercury-Vx300 spectrometer in CDCl$_3$ solvent containing TMS as an internal standard. Infrared spectrum (IR) was scanned in the range 4000 to 400 cm$^{-1}$ with KBr pellets on a Nicolet NEXUS FT-IR 5700 spectrophotometer. Melting points were measured on a WRS-1B micro melting point apparatus. A yellow solid appeared after 2–3 days for C$_3$H$_4$O (3.0 mmol) in 30 mL anhydrous alcohol. The resulting solution was concentrated to about 20 mL through reduced pressure distillation and then stood at room temperature. A yellow solid appeared after 2–3 days with the solvent evaporation. The solid was filtered off and washed with anhydrous alcohol three times and air-dried.

Syntheses of the complexes. Zinc(II) chloride (1.0 mmol) in 20 mL anhydrous alcohol was added dropwise to a hot solution of a Schiff base ligand (1.0 mmol) in 20 mL anhydrous alcohol. Thereafter the mixture was refluxed for about 2 h and then kept at room temperature for overnight and complex precipitates were filtered off and dried. The yields were 58% for I and 62% for II.

For C$_{38}$H$_{48}$N$_2$O$_2$Cl$_4$Zn (I) (M = 771.99)

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<tr>
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<th>C (%)</th>
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<tr>
<td>Found, %</td>
<td>C, 59.12; H, 6.27; N, 3.63.</td>
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Found, %: C, 58.97; H, 6.16; N, 3.51.

For C$_{40}$H$_{54}$N$_2$O$_4$Cl$_2$Zn (II) (M = 763.15)

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<th>C (%)</th>
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<tr>
<td>Found, %</td>
<td>C, 62.95; H, 7.13; N, 3.67.</td>
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Found, %: C, 62.70; H, 6.89; N, 3.63.

The molar conductance values ($\Lambda_m$) are 6.10 and 8.64 S cm$^2$ mol$^{-1}$ for I and II, respectively, which belong to the complex type of non-electrolytes molecular [17].

X-ray structure determination. Suitable crystals of I and II were grown by slow solvent evaporation of anhydrous alcohol. Diffraction data were collected on a Bruker Smart Apex II CCD with graphite monochromated MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å) at 298(2) K using the o-scan technique. The data were integrated by using the SAINT program, which also corrected the intensities for Lorentz and polarization effect [18]. An empirical absorption correction was applied using the SADABS program [19]. The structures were solved by direct methods using the program SHELXS-97 and all non–hydrogen atoms were refined anisotropically on $F^2$ by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package [20]. The hydrogen atoms were generated geometrically. All calculations were performed on a personal computer with the SHELXL-97 crystallographic software package. The details of the crystal parameters, data collection and refinement are summarized in Table 1. Selected bond lengths and angles with their estimated standard deviations are given in Table 2. The molecular structures, as shown in Fig. 1, were visualized by Diamond [21].

Supplementary material for complexes I and II has been deposited with the Cambridge Crystallographic Data Centre (nos. 886789 (I), 853684 (II); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The main IR data for I and II are given in Table 3, wherein several main data for ligands are also provided for comparison. Broad and intensity absorptions at 3433–3449 cm$^{-1}$ for ligands and complexes can be identified as $\nu$(O–H) indicating that phenolic hydroxyls of ligands are not deprotonated when the complexes are formed. The strongest absorptions at 1632 and 1621 cm$^{-1}$ for ligands as well as 1648 and 1643 cm$^{-1}$ for metal complexes these bands undergo upward shift by 15 and 20 cm$^{-1}$. The spectra of the ligands show strong bands at 1279 cm$^{-1}$ for L$_1$ and 1221 cm$^{-1}$ for L$_2$, which is fairly certain to $\nu$(C–O). In the complexes, this vibration band occurs at slight lower frequency with 1235 cm$^{-1}$ for I and with 1214 cm$^{-1}$ for II. The absorptions at 483 and 496 cm$^{-1}$ for I and II are attributed to $\nu$(Zn–O), indicating that oxygens of the Schiff bases are coordinated to Zn.