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SYNTHESIS AND STRUCTURAL STUDIES ON ZINC(II) MACROCYCLIC AND HETROCYCLIC COMPLEXES DERIVED FROM SCHIFF BASE AND MIXED LIGANDS OF 1,4-DIHYDROQUINOXALINE-2,3-DIONE, ORTHOPHENYLENE DIAMINE AND HYDROQUINONE

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ABSTRACT. In this study two new zinc(II) complexes involving oxygen and nitrogen donor sequences derived from 1,4-dihydroquinoxaline-2,3-dione (QXD), *o*-phenylenediamine (OPD) and hydroquinone (HQ) were synthesized through a template procedure. The structural elucidation of these complexes was carried out using measurement of molar conductance in 1x10^{-3} M solution of DMSO and various spectral techniques; ^{1}H and ^{13}C NMR, FT-IR, UV-VIS and AAS. The results showed that the zinc(II) ion coordinates with the Schiff base ligands in octahedral geometry, leading to the formation of stable macrocyclic and heterocyclic structures. The cyclic ligand (L) was found to coordinate as NNNN donor, through four imine nitrogen atoms which were formed up on condensation of the –NH_2 groups on *o*-phenylenediamine with C=O group on quinoxaline dione in a 2:2 mole ratio, in the presence of one mole equivalent of $ZnCl_2$ in ethanol medium. It also indicates the formation of a new mixed ligand zinc(II) complex with an OO OO O O coordination around zinc(II). The study contributes to the understanding of the coordination chemistry of zinc(II) with Schiff bases and provides insights into the development of novel zinc-based complex compounds.

KEY WORDS: Macrocyclic and mixed ligand, 1,4-Dihydroquinoxaline-2,3-dione, *o*-Phenylenediamine, Hydroquinone

INTRODUCTION

Organometallics and metal-organics are two major areas which have made immense contribution to coordination chemistry. Ligands derived from heterocyclic compounds containing hetero atoms such as N, O, S, P, and As have significantly enriched metal-organic complexes. The coordination chemistry of Zn(II) has been a subject of extensive research due to its significant role in biological systems and its versatile applications in catalysis, material science, and medicines. A large number of N-hetrocycles such as pyridines [1], bipyridyls, phenanthrolines [2], pyrazines, triazines, imidazoles [3], thiazoles, quinoxalines; containing appropriately oriented metal binding substituents such as -OH, -NH_2, -$NHNH_2$, -CHO, -$COCH_3$, -COOH, $CONH_2$ and their derivatives have been extensively used in the synthesis of metal chelates and their applications [4-7]. Zn(II) complexes are known for their ability to form stable complexes with a wide range of ligands, including Schiff bases, which are versatile ligands derived from the condensation of primary amines and carbonyl compounds.

Schiff base complexes of Zn(II) have attracted considerable attention because of their potential applications in catalysis, antibacterial and antifungal activities, and as models for metalloenzymes. In these complexes electronic redistribution between metal and ligand as a consequence of sigma- and pi-interactions; resonance and tautomeric preferences; hydrogen bonding and association interactions, metal-metal interactions and many such physical phenomena have resulted in characteristic structural, spectral, electrical, thermal, catalytic and magnetic properties [8].

Quinoxalines are N-heterocyclic compounds in which a benzene ring is fused to a six membered heterocyclic system containing two N-atoms in mutually para- disposition. Transition

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*Corresponding authors. E-mail: negash.getachew@aau.edu.et metal complexes of quinoxaline-1,4-dioxide [11], quinoxaline-2,3-dithione [12], quinoxaline-2,3-dicarboxylic acid [13] were initially investigated for complexation. Quinoxalines derived interest in view of their wide range biological applications. They are documented for pesticidal, herbicidal, insecticidal, antibiotic, anti-amebic, mutagenic, anti-helminthic, antileukemia properties. Quinoxaline-2,3-dione is interesting from coordination chemistry point of view. It has two ring N-atoms and two exocyclic O-atoms and can exhibit tautomerism due to mobile hydrogen atoms which can migrate to exocyclic oxygens and back based on experimental conditions, more significantly in solution. This can influence the chemistry of quinoxaline-2,3-dione and its derivatives. In view of this several derivatives of substituted quinoxalines and particularly those of quinoxaline-2,3-dione have been investigated [14].

Metal complexes play an important role as homogenous industrial catalysts, chemical vapor deposition, supramolecular chemistry, redox sensing, photo-physics, magnetic materials and they are essential in several biochemical process [15]. Mixed ligand complexes act as active catalysts in reactions of industrial importance including hydrogenation, hydroformation and oxidative hydrolysis of olefins and carboxylation of methanol. Chelating ligands containing O, N and S donor atoms show broad spectrum of biological activities and are of special interest in the variety of ways in which they are bonded to metal ions [16-19]. Schiff base Zn(II) complexes have gained considerable attention because of their applications in catalysis, antibacterial and antifungal activities. In this context, 1,4-dihydroquinoxaline-2,3-dione, *o*-phenylenediamine, and hydroquinone are fascinating ligands due to their ability to form conjugated systems with potential for strong coordination with zinc(II) ions.

Therefore, present research work includes studies on Zn(II) complexes in two different chemical environments employing quinoxaline-2,3-dione. Zn(II) ion has been chosen in view of its versatility in coordination geometries and biological importance. This research, however, deals only with the synthesis and characterization of these complexes. Several d-metal ions and their complex compounds have been studied by other investigators [20-23]. Here, we report the detailed synthesis, characterization, and structural studies of these Zn(II) complexes using various spectroscopic techniques, including UV-Vis, FT-IR, and NMR. The findings from this study contribute to a better understanding of the coordination behavior of Zn(II) with Schiff base ligands and open up new possibilities for the design of zinc-based functional materials.

EXPERIMENTAL

Chemicals and reagents

All the chemicals and solvents used in this work were obtained from Aldrich Chemical Company. The chemicals used for the synthesis of metal complexes were of analytical grade including, anhydrous zinc chloride ($ZnCl_2$, 99.5%) oxalic acid dihydrate ($C_2H_2O_4.2H_2O$, 99.9%), hydroquinone ($C_6H_6O_2$, 95%) and *o*-phenylenediamine ($C_6H_8N_2$, 98.5%). Nitric acid (HNO_3, 69%) and solvent such as methanol (CH_3OH, 97%), ethanol (CH_3CH_2OH, 99%), acetone (CH_3COCH_3, 99.5%), dimethylsulfoxide (DMSO, 98.5%), dimethylformamide (DMF, 99%) and chloroform ($CHCl_3$, 99%).

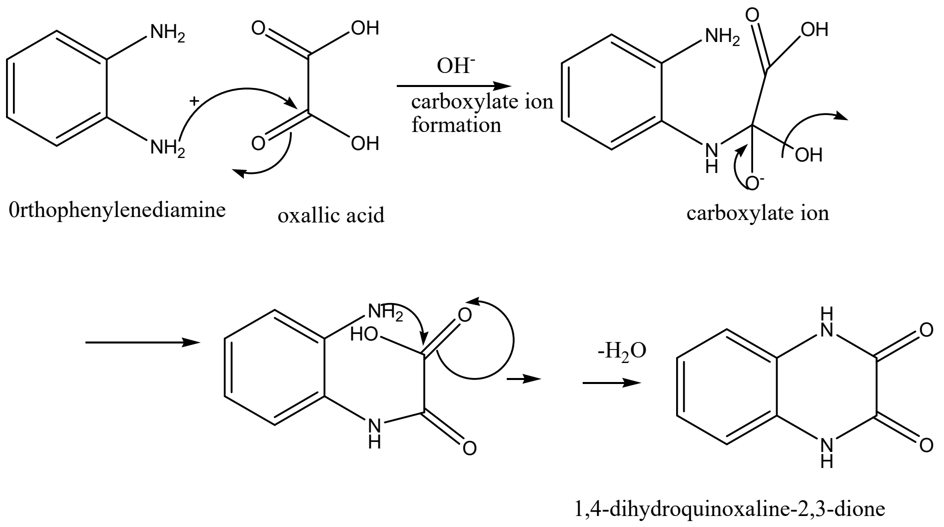
Apparatus and instruments

Fourier-transform infrared (FT-IR) spectral data were recorded using Perkin Elmer 65 FT-IR Spectrophotometer. Buck Model Scientific 210 VGB atomic absorption spectrometer (AAS) was used for the metal determination. The nuclear magnetic resonance (NMR) data were recorded on a Bruker Avance III HD 600 spectrometer. Electronic spectra of the prepared complexes were measured in the region of 200–800 nm using 10^{-3} M solutions in dimethyl sulfoxide (DMSO) at 25 °C using the Shimadzu UV-160A ultraviolet-visible (UV-Vis) spectrophotometer with a 1.0

cm matched quartz cell. Electrical conductivity measurements of the complexes were recorded at room temperature using 1.0 x 10^{-3} M sample solutions in DMSO using a PW9527 digital conductivity meter (Philips). Melting points were recorded using the Stuart melting point apparatus.

Synthesis of 1,4-dihydroquinoxaline-2,3-diones

Orthophenylenediamine (5.5 g), oxalic acid (6.5 g) and 4 N HCl (30 mL) were heated to boiling for 15 min. A crystalline solid was formed. The reaction mixture was cooled and the solid was collected, washed with water and dried. The compound obtained was dissolved in alkali and then acidified with HCl, so that, the pure compound was obtained. Yield: 3 g, m.p > 370 °C [19=15].



Scheme 1. Proposed mechanism for the synthesis of 1,4-dihydroquinoxaline-2,3-dione.

Synthesis of the complex compound, $ZnC_{28}H_{22}N_4O_8$

To an aqueous solution (10 mL) of Zn(II) chloride anhydrous (1 mmol, 0.14 g), hot ethanoic solution (10 mL) of 1,4-dihydroquinoxaline-2,3-dione (2 mmol, 0.324 g) was added. The mixture was stirred and kept in a boiling water bath for 10 min. To this hot solution, ethanoic solution, 10 mL of hydroquinone (2 mmol, 0.220 g) was added with constant stirring. The mixture was refluxed for 4 hours in a water bath. The complex was obtained by raising pH of the reaction mixture to 7.5 by adding 0.5% sodium hydroxide solution. The mixture was cooled and solid complex obtained was filtered, washed with water followed by ethanol. The complex was white in color.

Synthesis of complex compound, $ZnC_{28}H_{20}N_8Cl_2$

To an aqueous solution (10 mL) of zinc(II) chloride anhydrous (0.14 g), a hot ethanoic solution (10 mL) of 1,4-dihydroquinoxaline-2,3-dione (0.324 g) was added. The mixture was stirred and kept in a boiling water bath for 40 min. To this hot solution, hot ethanoic solution (10 mL) of *o*-phenylenediamine (0.216 g) was added with constant stirring. The mixture was refluxed for 7 hours in a water bath. The complex was obtained by adjusting the pH of the reaction mixture in the range 6.0-7.5, through the addition of 0.5% sodium hydroxide solution. The mixture was then cooled and solid complex obtained was filtered, washed with water followed by ethanol. The complex was white grey in color [24]. Yield 59.99% and the melting point is 366 °C. The possible chemical reaction is:

$$\mathrm{ZnCl_2(aq) + 2C_8H_6N_2O_2(EtOH)} \xrightarrow[\text{reflux 7 hr and 40 min}]{\mathrm{2C_6H_8N_2(EtOH)}} \mathrm{ZnC_{28}H_{20}N_8Cl_2}$$

$$\mathrm{ZnCl_2\,(aq)} \quad + \quad \mathrm{2C_8H_6N_2O_2\,(EtOH)} \xrightarrow[\text{reflux}]{\text{10 min}} \xrightarrow[\text{reflux 4 hour}]{\mathrm{2C_6H_6O_2\,(EtOH)}} \mathrm{ZnC_{28}H_{22}N_4O_8}$$

Scheme 2. The reactions for the synthesis of $\mathrm{ZnC_{28}H_{22}N_4O_8}$ (top) and $\mathrm{ZnC_{28}H_{20}N_8Cl_2}$ (bottom).

Solubility measurements

The powder sample was directly added to seven test tubes containing methanol, ethanol, DMSO, water, chloroform, acetonitrile, and n-hexane in order to check which solvent can dissolve the sample and also to identify the best solvent for the analytical and spectroscopic measurement.

Melting point measurements

An electrothermal melting point apparatus was used to measure the melting point of the crystal sample.

TLC analysis

A 0.04 g of the sample was measured and dissolved in DSMO. The solution was added into the beaker and then the silica gel coated aluminum plate was placed in it to identify the purity of the sample.

Molar conductivity measurements

EC-214 Conductivity meter (HANNA Instrument) was used to measure the molar conductance of the sample in solution. A 0.04 g of sample was dissolved in DMSO to form 1×10^{-3} M solution.

*FT-IR measurement*s

Perkin Elmer 65 FT-IR Spectrophotometer was used for recording the FT-IR spectra with KBr pellets in the range of 400 - 4000 $\mathrm{cm^{-1}}$.

Atomic absorption spectrometry measurements

The metal content of each sample was determined by using Buck Model Scientific 210 VGB atomic absorption spectrometer (AAS). Percentage was estimated by dissolving 0.04 g of each zinc complex in 10 mL of DMSO. Different volumes of the clear solution were appropriately diluted into 50 mL volumetric flasks to make solutions of known concentrations of the complex.

Electronic UV-Vis spectra measurements

UV-T-60, UV-Vis spectrometer was used to record the electronic spectra of the complexes in the wave length range 200-800 nm. The sample measured was prepared in the form of solution and its concentration was 1.4x10^{-3} M in DMSO at 22 °C temperature.

RESULTS AND DISCUSSION

The $ZnC_{28}H_{20}N_8Cl_2$ and $ZnC_{28}H_{22}N_4O_8$ complexes were obtained as powders with high melting points and low solubility in organic solvents. Both complexes are colored. They were air and moisture stable solids and were soluble in DMSO. Based on the analytical data the formulae $ZnC_{28}H_{20}N_8Cl_2$ and $ZnC_{28}H_{22}N_4O_8$ were adjudged for $ZnC_{28}H_{20}N_8Cl_2$ and $ZnC_{28}H_{22}N_4O_8$, respectively. The formulae support a 2:2 molar condensation of 1,4-quinoxaline-2,3-dione and *o*-phynalenediamine to form $ZnC_{28}H_{20}N_8Cl_2$, a macrocyclic complex, wherein L is a neutral cyclic ligand. The quantitative estimation of the complexes indicated the presence of chloride in $ZnC_{28}H_{20}N_8Cl_2$ (M:Cl in 1:2 ratio) and the absence of chloride in $ZnC_{28}H_{22}N_4O_8$.

Molar conductivity studies

The complexes were dissolved in DMSO and the molar conductivities of 1x10^{-3} M solutions at 22 °C were measured. The measured values are lower than those expected for an electrolyte. These observations indicate that the complexes are non-electrolytes in DMSO (10^{-3} M) at room temperature. The measured values are given in Table 1.

As the complex $ZnC_{28}H_{20}N_8Cl_2$ was a non-electrolyte, it is suggested that the chlorides occupied the coordination sphere. The non-electrolyte behavior and absence of chloride in $ZnC_{28}H_{22}N_4O_8$ suggest deprotonation of one of the ligands to neutralize the zinc ion. Matching with the pH of the medium maintained during the isolation of the complex (7.5), it is proposed that each coordinated hydroquinone molecule underwent deprotonation of one phenolic hydroxyl group, while 1,4-dihydroxyquinoxaline-2,3-dione molecules behaved as neutral donors. The spectral data provided support for these conclusions.

Metal determination in complexes by atomic absorption spectroscopy

The metal percentage was estimated by decomposing 10 mg of the metal complex through digestion in 10 mL conc. HNO_3 until a clear solution was observed. The clear solution was diluted in 50 mL volumetric flask to make solutions of known concentration. In the case of $ZnC_{28}H_{20}N_8Cl_2$, the known solution again diluted by 10 mL, and in the case of $ZnC_{28}H_{22}N_4O_8$, the known solution again diluted by 80 mL, finally the metal content was recorded using atomic absorption spectrometer, Table 1.

The metal estimation indicated the approximate relation between the calculated and the theoretical mass of zinc ions in the two complex compounds.

Table 1. Molar conductivity and atomic absorption spectroscopy values of the complexes.

Solvent	Complexes	Molar conductivity ($\Omega^{-1}cm^2mol^{-1}$)	Theoretical conc. (% Zn)	Experimental conc. (% Zn)
DMSO	$ZnC_{28}H_{22}N_4O_8$	3.45	10.77	9.144
DMSO	$ZnC_{28}H_{20}N_8Cl_2$	2.18	10.82	13.38

Infrared spectrum of 1,4-dihydroquinoxaline-2,3-dione (QXD)

The FT-IR spectrum of the 1,4-dihydroquinoxaline-2,3-dione (QXD) showed three characteristic bands at 3443, 1392 and 1682 cm^{-1} that are the regions for stretching vibration, υ(N-H), υ(C-N) and υ(C=O), respectively. The bands at 3047, 2882 and 2865 cm^{-1} are in the characteristic regions of υ(C-H) stretching vibration of benzene. The bands at 753 and 855 cm^{-1} are the characteristics of out plane bending vibration of (C-H) in benzene (Figure 1) [25].

Infrared spectrum of $ZnC_{28}H_{22}N_4O_8$

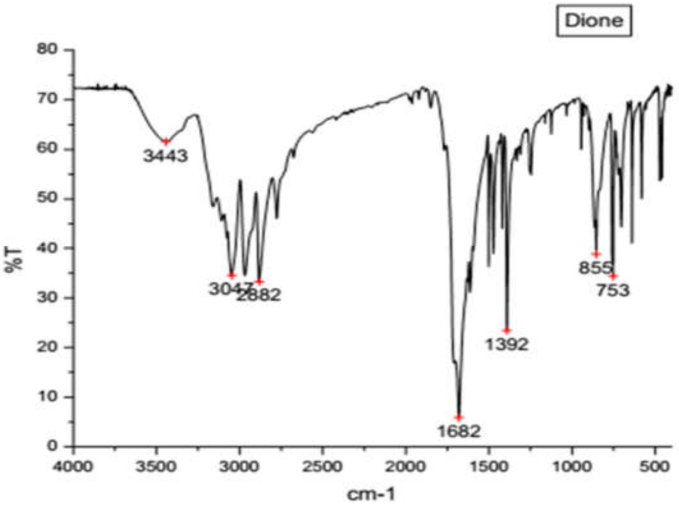
Based on the composition of the complex and other experimental data it is assumed to be a mixed ligand complex. In order to study the binding modes of the ligands to the metal ion in the complex, the FT-IR spectra of the free ligands were compared with the FT-IR spectrum of the complex. In the spectrum of the complex the band at 1688 cm^{-1} is for υ(C=O) as compared with υ(C=O) of 1,4-dihydroquinoxaline-2,3-dione at 1682 cm^{-1}. This indicates the coordination of exocyclic carbonyl on 1,4-dihydroquinoxaline-2,3-dione in trans-arrangement around the Zn(II) and the hydrogen bond strength is more affected in the case of complex molecule [26]. The three characteristic bands at 3049, 2967 and 2865 cm^{-1} are the characteristic stretching vibration of (C-H) in the benzene of 1,4-dihydroquinoxaline-2,3-dione as well as of hydroquinone. The –OH vibrations are generally measured between (3600-3200 cm^{-1}). The band observed at 3362 cm^{-1} for the complex falls in is the characteristic region of (-OH) stretching (Figure 1) in hydroquinone [25]. It is to be recalled that the bonded hydroquinone in this complex possesses one deprotonated and one free hydroxyl group. Free hydroquinone is expected to exhibit intermolecular hydrogen bonding, which can lower the stretching frequency and broaden the band structure.

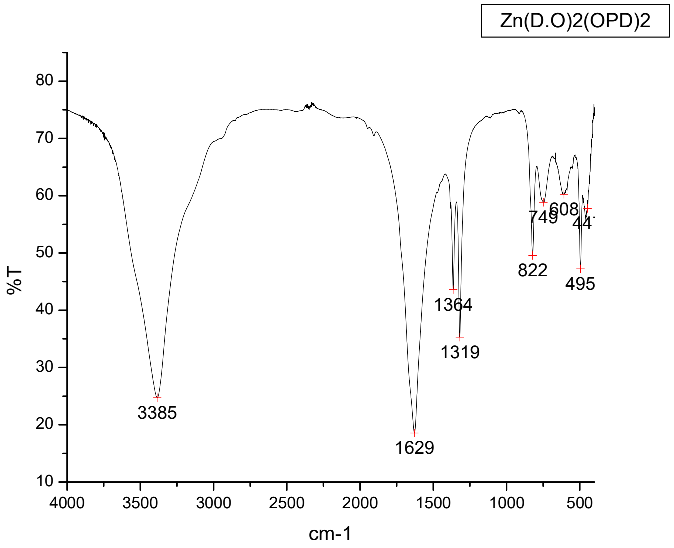
Intermolecular hydrogen bonding due to free hydroxyl functions as depicted in Figure 1 is also possible in the complex, which could be the reason for lower ν(O-H) in the complex. The medium intensity bands observed at 1200-1225 cm^{-1} are assigned to ν(C-O) of free and deprotonated hydroxyl groups respectively in the complex. The band observed at 1411 cm^{-1} is the characteristic region for stretching vibration of both (C-C) and (C=C), because the two functional group are called semicircle stretching vibration, usually occur in the region 1625-1400 cm^{-1}. The band observed at 1193 cm^{-1} is the characteristic region for stretching vibration of (C-N) in 1,4-dihydroquinoxaline-2,3-dione. The band observed at 766 cm^{-1} is the region for out plane bending vibration of (C-H) in benzene ring and hydroquinone [27]. The far FT-IR spectra show bands in the region 584-464 cm^{-1} corresponding to Zn-O vibrations (Figure 1).

Infrared spectrum of $ZnC_{28}H_{20}N_8Cl_2$

A typical new strong band located at 1629 cm^{-1} in the spectrum of the complex assignable to C=N stretching confirmed the condensation reaction between 1,4-dihydroquinoxaline-2,3-dione and *o*-phenylenediamine. The condensation of carbonyl groups of 1,4-dihydroquinoxaline-2,3-dione and amino groups of *o*-phenylenediamine in a 2:2 mole ratio in the presence of Zn(II) has resulted in the formation of a cyclic ligand (Figure 1).

This is a typical metal ion promoted template reaction. The free cyclic ligand could not be isolated due to strain associated with the 12-membered rings [28]. Metal chelates can stabilize such rings due to modified ring size. The unstable free 12 membered hetero cyclic compound gains stability with the introduction of Zn(II), due to the popular chelate effect. The template synthesis promotes the formation of stable 5-membered metallo-cycles. The 12-membered ring gets modified into a chelate containing four 5 membered metallo-cycles. In the presence of divalent zinc, a quadra dentate cyclic system is formed which coordinates through four imine nitrogen atoms (Scheme 3). The metal complex assumes symmetric macrocyclic geometry in the XY- plane. The broad band at 3385 cm^{-1} in the spectrum of the complex is assigned to ν(N-H) on quinoxaline moiety [27]. Lowering of ν(N-H) in the spectrum of the complex is attributed to hydrogen bonding. The far FT-IR spectra (Figure 1) show bands in the region 495 cm^{-1} to 444 cm^{-1} corresponding to υ(Zn-N) vibrations (Table 2).





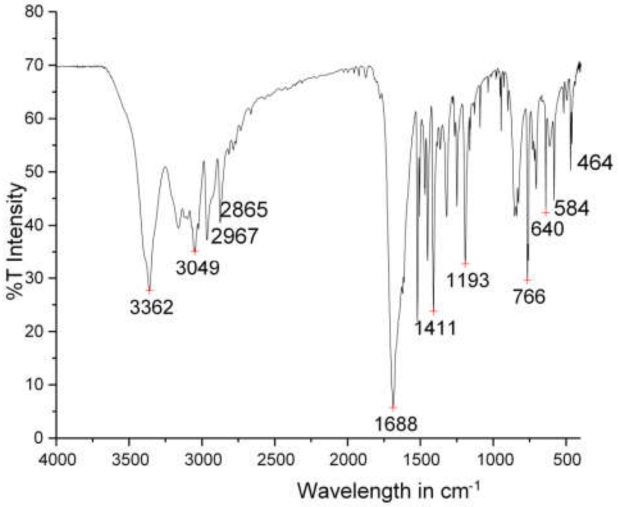


Figure 1. The FT-IR spectra of 1,4-dihydroquinoxaline-2,3-dione, $ZnC_{28}H_{22}N_4O_8$ and $ZnC_{28}H_{20}N_8Cl_2$.

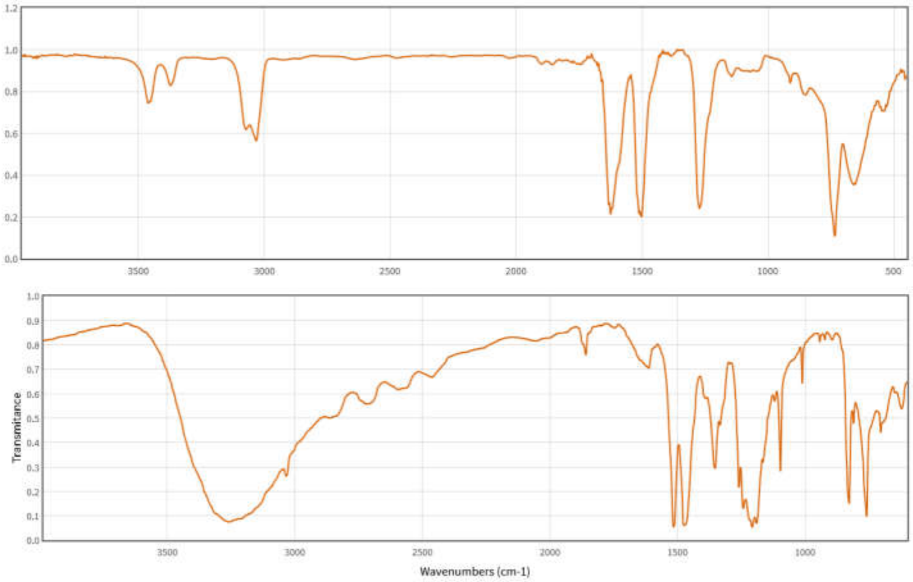


Figure 2. IR spectra of *o*-phenylenediamine (top) and hydroquinone (bottom).

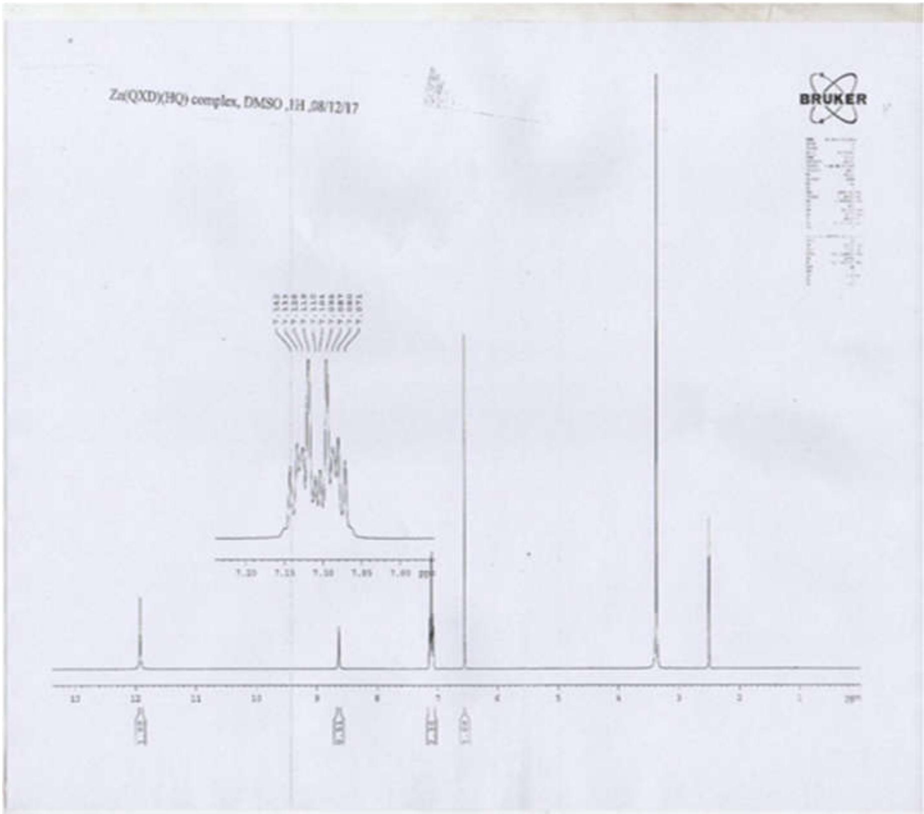
Two diagnostic features are displayed in the spectrum: (1) the typical two band pattern due to anti-symmetric and symmetric stretching of amine functions of *o*-phenylenediamine (Figure 4) are absent in the spectrum of the complex and (2) the characteristic intense band of quinoxalinedione is also absent in the spectrum of the complex.

Table 2. FT-IR data of the ligands (QXD and HQ) and the complexes, $ZnC_{28}H_{22}N_4O_8$ and $ZnC_{28}H_{20}N_8Cl_2$.

Compounds	υ(C-H) cm^{-1}	υ(O-H) cm^{-1}	υN-H cm^{-1}	υC=O cm^{-1}	υC=N cm^{-1}	υC-N cm^{-1}	υC=C cm^{-1}	υC-O cm^{-1}	υM-O cm^{-1}	υM-N cm^{-1}
QXD	2882 - 3047	-	3443	1682	-	1392	1411	-	-	-
HQ	3100 - 3000	3600 - 3200	-		-	-	1680- 1640	1250- 1050		
$ZnC_{28}H_{20}N_8Cl_2$	-	-	3385	-	1629	1364 - 1319	1411	-	-	444 - 495
$ZnC_{28}H_{22}N_4O_8$	2865 - 3049	3362	3362	1688	-	-		1193	464 - 584	-

^{1}H-NMR of $ZnC_{28}H_{22}N_4O_8$

The ^{1}H NMR spectrum of the complex (Figure 3) shows multiple signals observed at δ 7.071-7.142 ppm that may be attributed to aromatic protons on quinoxalinedione (QXD). The signal at δ 6.5 is due to aromatic protons singly deprotonated hydroquinone. The singlet observed in the region 12 ppm may be assigned to -NH protons of the quinoxaline. The signal observed at 8.51 ppm corresponds to O-H proton on the mono negative hydroquinone anion. The chemical shifts, signal intensities and integral strengths support the formation of the Zn(II) complex [28].



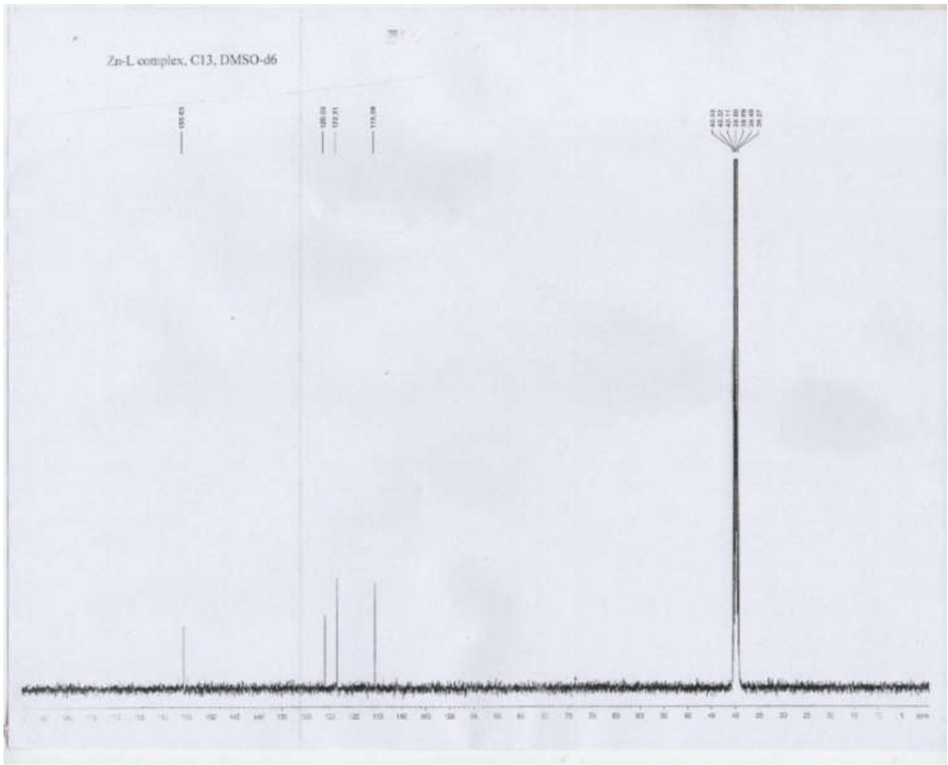


Figure 3. ^{1}H-NMR and ^{13}C-NMR spectra of the complex compound, $ZnC_{28}H_{22}N_4O_8$.

^{13}C NMR of $ZnC_{28}H_{22}N_4O_8$

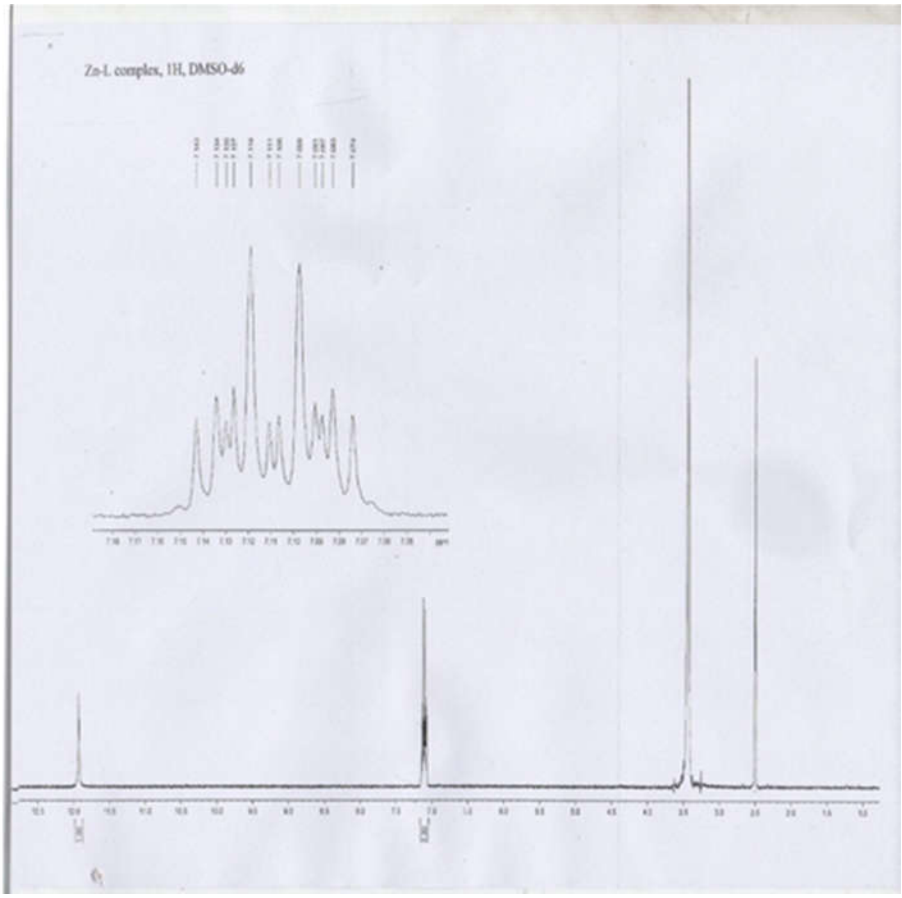
The ^{13}C NMR spectrum of the ligand (QXD) and the complex (Figure 3), $ZnC_{28}H_{22}N_4O_8$ displays resonances at 40, 115.58, 116.10, 123.47, 126.05, 150.18 and 155.62 ppm that are attributed to CH_3(DMSO), C=C (Ar-), C=C (HQ),C-N, and C=O groups respectively. However, it was not possible to get a resolved spectrum because of the solubility of the complex.

^{1}H-NMR of $ZnC_{28}H_{20}N_8Cl_2$

The ^{1}H NMR spectrum of the complex (Figure 4) shows a singlet at 12 ppm which is assigned to -NH protons on quinoxaline. A complex multiplet at 7.074-7.143 ppm region is attributed to C-H protons. Absence the signals due to protons on amine functions of o-Phenylenediamine support condensation of these amine groups and exocyclic carbonyl groups in the presence of Zn(II) to form the macrocyclic complex [28].

^{13}C-NMR $ZnC_{28}H_{20}N_8Cl_2$

The ^{13}C NMR spectrum of the complex is shown on Figure 4, displays resonance at 40, 115.59, 123.51, 126.03 and 155.63 ppm that is attributed to CH_3(DMSO), C=C-(Ar), C-N (pyrazine ring) and C=N(imine) group, respectively. Absence of any signal characteristic of exocyclic carbonyl further supports the condensation reaction between quinoxaline dione and o-Phenylene diamine in the presence of Zn(II) and formation of the macrocyclic chelate [29].



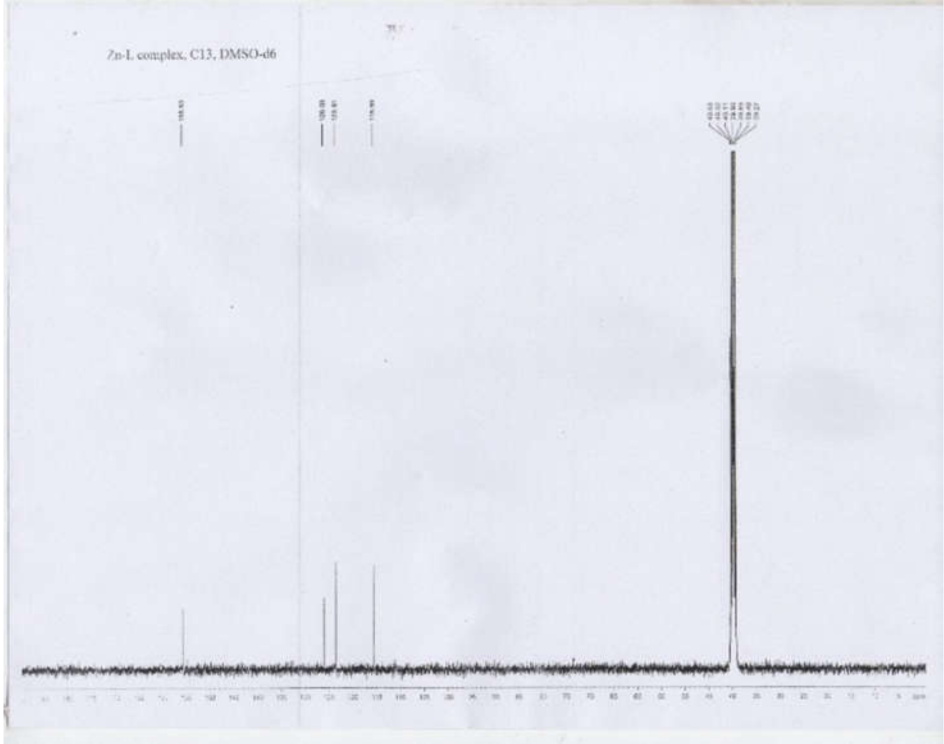


Figure 4. ^{1}H-NMR and ^{13}C-NMR spectra of the complex compound, $ZnC_{28}H_{20}N_8Cl_2$.

Electronic spectrum of $ZnC_{28}H_{22}N_4O_8$

The electronic spectrum of the complexes is shown in Figure 5. The bands at 298 nm and 249.50 nm are assigned to n-π* transition of carbonyl group and π-π* transition of benzene ring, respectively. The absorption at 295 nm, 98 nm and 321.5 nm could be assigned to a charge transfer transition. The blue color of the complex may be conjured as having arisen from this absorption in the ultraviolet region.

Electronic spectrum of $ZnC_{28}H_{20}N_8Cl_2$

As expected from a d^{10} electronic configuration, the electronic spectrum of $ZnC_{28}H_{20}N_8Cl_2$ (Figure 5) complex does not show any d-d transition. The two transition in the electron spectrum of the ligands are n-π* (transition that shifts to shorter wave length) that is attributed to the interaction with the solvent, and π-π* (transition that shifts to longer wave length). The observed bands are due to the ligand and charge transfer transitions, i.e. the bands at 296.5 nm and 250 nm that are assigned to n-π* transition of imine (C=N) and π-π* transition of benzene ring, respectively. These transitions are also found in the spectra of Zn-L complexes i.e. since zinc ion has d^{10} configuration, the absorption at 294.5 nm, 296.50 nm and 320.50 nm could be assigned to a charge transfer transition [30].

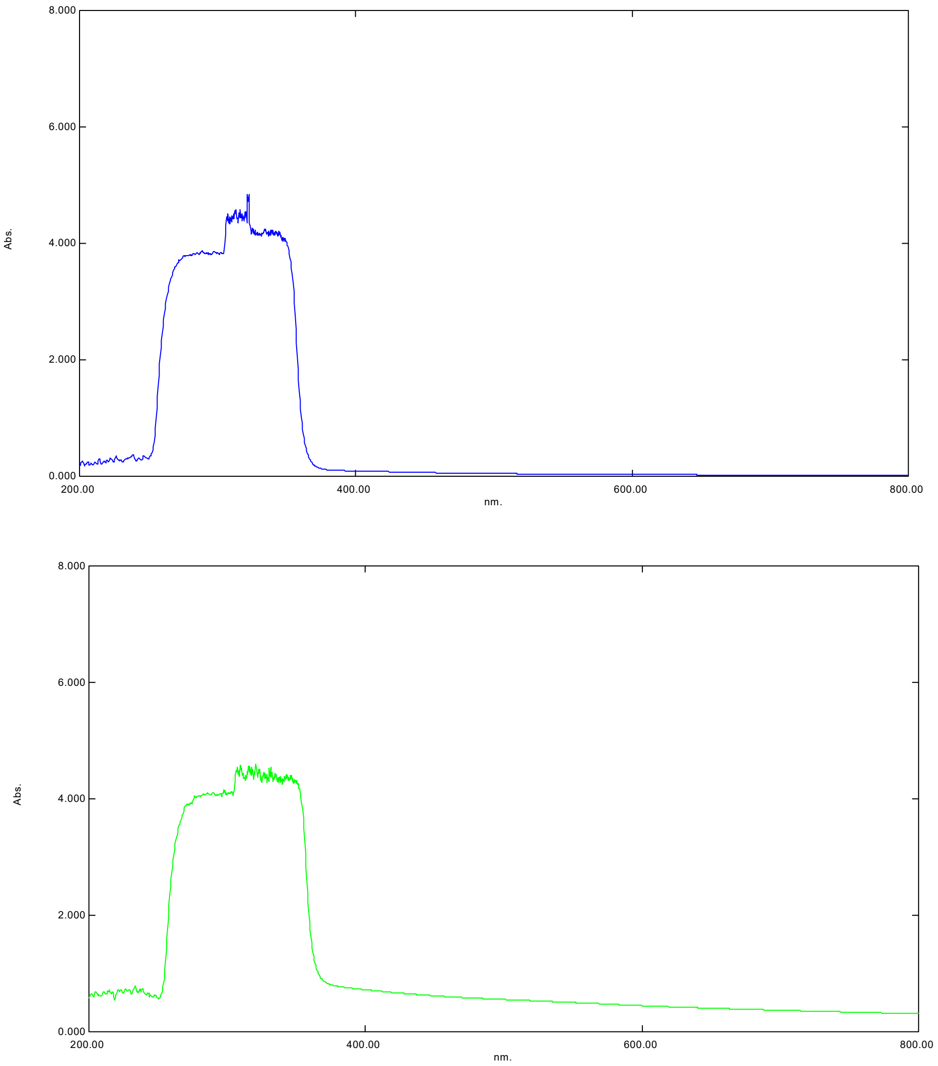
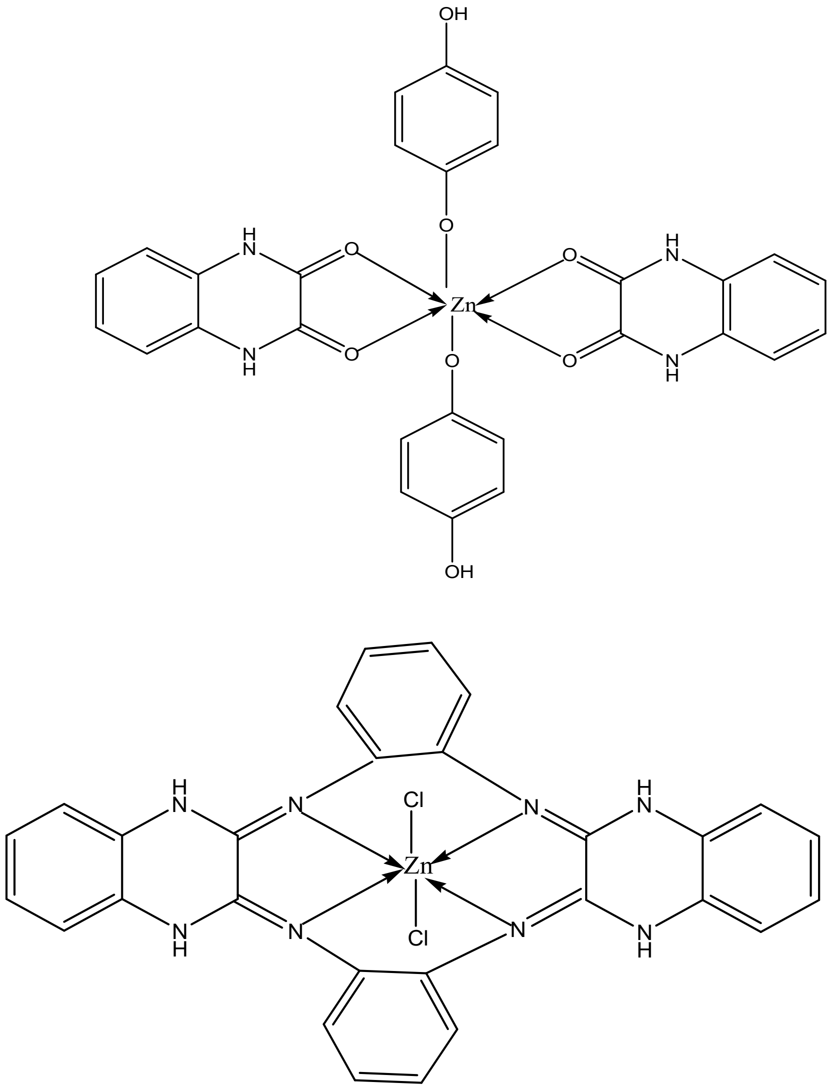


Figure 5. UV-VIS spectra of $ZnC_{28}H_{22}N_4O_8$ (top) and $ZnC_{28}H_{20}N_8Cl_2$ complex (bottom).

The proposed octahedral complexes $ZnC_{28}H_{22}N_4O_8$ (top) and $ZnC_{28}H_{20}N_8Cl_2$ (bottom) are represented in Scheme 3.



Scheme 3. The suggested structures of the synthesized complex compounds, $ZnC_{28}H_{22}N_4O_8$ (top) and $ZnC_{28}H_{20}N_8Cl_2$ (bottom).

CONCLUSION

Two Zn(II) complexes with novel structural features were synthesized and characterized. One of them is a mixed ligand complex ($ZnC_{28}H_{22}N_4O_8$) and the other is a chelate containing a new macrocyclic ligand ($ZnC_{28}H_{20}N_8Cl_2$). The new macrocyclic ligand was obtained from 2:2 mole condensation of *o*-phynalenediamine and 1,4- dihydroxyquinoxaline-2,3. Analytical, conductivity and spectral studies support the formation of octahedral complexes. The results showed Zn(II) ions coordinate effectively with the Schiff base and mixed ligands, forming stable and well-defined macrocyclic and heterocyclic complexes. It is interesting to note that ZnL’$_2$ L”$_2$ (L’= quinoxalinedione and L” = mono negative 1,4-hydroquinone) has OO OO O O coordination due to two 1,4-dihydroquinoxaline-2,3-dione ligand molecules and two mono deprotonated hydroquinone ions. ZnLCl$_2$ (L = macrocyclic ligand) is macrocyclic chelate consisting of four five membered metallo-cycles. Preparation of free ligand L was not feasible; however the complex synthesis was accomplished through template process. The insights gained from this research contribute to the growing body of knowledge on zinc complexes paving the way for future research and development.

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