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Synthesis and characterization of N, N′-bis (isatin) diamino zirconium (IV) complexes

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Abstract

N, N′-bis (isatin) diamine schiff base ligands were synthesized by the condensation reaction of Isatin with various diamine (ethane-1,2-diamine, propane-1,3-diamine and hexane-1,6-diamine) in 2:1 molar ratios. These ligands were used to prepare Zr (IV) complexes. Prepared ligands and complexes were characterized by using conductance measurement, FT-IR, UV-Visible and ^{1}HNMR spectroscopy. The presence of FT-IR band for azomethine group supports the formation of ligand. Vibrational bands for Zr←N and Zr←O in complexes signify the coordination through O and N sites of ligands. ^{1}HNMR peak for NH moiety in ligand gets almost disappeared in complex reveals tautomerism of NH with nearby carbonyl oxygen due to the effect of complexation. The absence of peak above 500 nm in the electronic spectra indicates d^0 system of zirconium in complexes. The elemental analytical data was analogous to theoretical composition of ligands and complexes. The molar conductance values obtained for the complexes represent their non-electrolytic character.

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Introduction

1H-indole-2,3-dione, commonly known as Isatin, is one of the leading class of oxo-derivative indoles with synthetic versatility. It is used as building entity of a broad range of alkaloids, drugs, pesticides and dyes (Konstantinovic *et al.*, 2015). Isatin and its derivatives possess antimicrobial, antiviral, anticonvulsive, antitumor, anti-HIV, anti-inflammatory and antimycobacterial activity (Mathur and Nain, 2014). It acts as potent antagonist on trial natriuretic peptide receptors in vitro (Sonawane and Tripathi, 2013). Therefore, medicinal and biological values of isatin have attracted the research community in developing ligand with effective capturing ability like Schiff bases. Schiff bases are used as substances in the preparation of a number of industrial and biologically active compounds *via* ring closure, cycloaddition and replacement reaction. On the industrial scale, they have wide range of applications such as dyes and pigments. Goyat *et al.* (2016) synthesized N, N'-Bis (indol -2-oxo-3-ylidene)-1, 2-Diaminoethane and N, N'-Bis (indol -2-oxo-3-ylidene)-1, 3-Diaminopropane Schiff base complexes of tellurium(IV) and found 92% and 91% inhibiting activity against *Mycobacterium tuberculosis* compared to Rifampin standard. Konstantinovic *et al.* (2015) synthesized of isatin-3-(4'-hydroxy) benzoylhydrazone and observed their inhibiting activity against the Gram-positive bacteria *Enterococcus faecalis* and yeast *Candida albicans* in the concentration range of 25-50 μg-cm. Ade *et al.* (2012) synthesized Dichloro-[4-Chloro-2-(2-oxo-1, 2-dihydro-indol-3-ylidene amino)-benzoic acid] (ACBAI) aquo complexes of Ti(IV), Zr(IV) and Cd(II) chloride and proposed uninegative tridentate nature of (ACBAI) ligand. Hakimi *et al.* (2011) synthesized (isatin-3-thiosemicarbazone) -bis- (triphenylphosphine) copper(I) nitrate and reported monoclinic structure of it. In the study of the production of 1, 2, 4-oxadiazole [4, 5-a] indolones, Jiang *et al.,* (2017) reported the lactam-lactim tautomerization of isatin depending on the nature of solvents.

Therefore, designing of new complexes of diamino isatin based Schiff base ligand still possess considerable research value. In the present work, we would like to synthesize

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zirconium(IV) complex of N, N′-bis (isatin) diamine schiff base ligands, where diamines are ethane-1,2-diamine, propane-1,3-diamine and hexane-1,6-diamine. As a bioactive element zirconium complexes have clinical importance. The isotope ^{89}Zr has been applied to the tracking and quantification of molecular antibodies with positron emission tomography (PET) camera (Rij *et al.,* 2011). Zirconium-containing compounds are used in many biomedical applications including dental implants and other restorative practices, knee and hip replacements, and middle-ear ossicular chain reconstruction (Lee *et al.*, 2010). Although, well defined experimental study on zirconium complexes stated above, N, N′-bis (isatin) diamine ligands with zirconium have not yet been done. In this context, the synthesis of N, N′-bis (isatin) diamino zirconium (IV) complex [ZrL^nCl_2] is considered as a new attempt.

Materials and methods

Some N, N′-bis (isatin) diamine type ligands were prepared by using isatin with diamines. The origin of ethane-1,2-diamine, propane-1,3-diamine and hexane-1,6-diamine used in this research were Scharlau, SPAIN; Isatin or [1H-indole-2,3-dione] from BDH, UK; Zirconyl Chloride ($ZrOCl_2.8H_2O$) from E.merck, Germany. Methanol and ethanol were used as supplied from Scharlau, Spain, DMSO from India and DMF from Guangdong, China. All of the chemicals and solvents were analytical grade and were used without further purification.

Preparation of N, N′-bis (isatin) diamine ligands

N, N′-bis (isatin) diamine ligands were prepared through the condensation reactions of isatin and diamines as in the reported procedure (Goyat *et al.,* 2016; Khalifa and Hassaan,1995). Isatin (2 mmol) was dissolved in 25 cm^3 hot methanol with continuous stirring and allowed to cool. Then 1 mmol diamine (ethane-1,2-diamine, propane-1,3-diamine and hexane-1,6-diamine) was introduced in the prepared methanolic solution of isatin. After that, the whole mixture was refluxed for three hours. Finally, the precipitate was obtained inside the reaction vessel. There after the precipitate was filtered off, washed with methanol and dried over silica gel in vacuum desiccators. The reaction for ligand preparation is shown in Scheme A.

Preparation of N, N′-bis (isatin) diamino zirconium (IV) complex [ZrL^nCl_2]

To prepare ZrL^nCl_2 (n=1, 2, 3) type N, N′-bis (isatin) diamino zirconium (IV) complex, 1 mmol of zirconyl chloride was dissolved in the 30 cm^3 ethanol. Then 1 mmol prepared ligand was added to this solution with constant stirring. After a complete stirring for three hours a reddish precipitate came out. This precipitate was filtered off, washed with ethanol and dried under vacuum over silica gel. A few drops of H_2SO_4 was added to the mixture to pace the precipitation of N, N′-bis (isatin)-1,2-diamino zirconium (IV) dichloride complex. Here, ZrL^1Cl_2, ZrL^2Cl_2 and ZrL^3Cl_2 denotes N, N′-bis(isatin)-1,2-diaminoethane zirconium (IV) complex, N, N′-bis (isatin)-1,3-diaminopropane zirconium (IV) complex and N, N′-bis (isatin)-1, 6-diaminohexane zirconium (IV) complex, respectively. The reaction for complex preparation is shown in Scheme B.

Analysis

Melting points, an important property of the ligands as well as of the complexes were performed by an Electro thermal Melting Point Apparatus of Stuart, model SMP 10, UK. The elemental analysis of ligands and complexes were done by CHEMMOL V1.0 analyzer and metal analysis by Shimadzu AA-7000, AAS using GFA-7000. Conductometer model HANNA (HI 2300) was used in conductivity measurements of prepared samples. N, N-dimethyl-formamide (DMF) was used as solvent for conductivity measurements. The FT-IR spectra were run on KBr pellet and recorded with FT-IR 8400S Shimadzu spectrophotometer in the range 4000-400 cm^{-1} at 2 cm^{-1} resolution and 30 times scanning. ^{1}H-NMR spectra of samples in DMSO solvent were run using BRUKER 400 MHz NMR spectrometer. Electronic absorption spectra were recorded on single beam Optizen UV Spectrophotometer in DMF solution using 1cm cell. Table I shows the physical data of the prepared ligands and complexes.

Results and discussion

Elemental analysis

The percentage of elements of Ligands (L^1, L^2 and L^3) and their corresponding Zr(IV) complexes are shown in Table I. The experimental results are comparable to the calculated values for the ligands (L^1, L^2 and L^3) and their respective Zr (IV) complexes. These indicate almost similar elemental composition of synthesized ligands and complexes to the expected structure.

Molar conductance

The electrolytic nature of the complexes can be obtained from their molar conductance (Λ) measurement. The molar conductance values of the prepared zirconium (IV) complexes of the N, N′-bis (isatin) diamine schiff base ligands found very low which is depicted in Table I. The low molar conductivity of all complexes suggest their

Table I. **Physical data, elemental analysis and conductance data of the prepared N, N′-bis (isatin) diamine Schiff base ligands (L^1, L^2 and L^3) and their zirconium complex [ZrL^1Cl_2], [ZrL^2Cl_2] and [ZrL^3Cl_2]**

Ligands	Physical data			Elemental analysis			Conductivity data
	Color	Yield %	m.p. (° C)	C% (Cal)	H% Cal	N% Cal	Molar conductance $ohm^{-1}cm^2 mol^{-1}$ (Solvent: DMF)
L^1	Deep Yellow	70	206	63.50 (67.92)	4.03 (4.40)	14.96 (17.61)	--
L^2	Yellow	72	190	69.46 (68.67)	4.88 (4.82)	14.77 (16.87)	--
L^3	Yellow	72	182	69.46 (70.59)	5.95 (5.88)	14.87 (14.97)	--
ZrL^1Cl_2	Red	76	222	31.86 (44.98)	2.48 (2.92)	8.73 (11.66)	12
ZrL^2Cl_2	Red	74	200	28.56 (46.13)	2.75 (3.24)	5.69 (11.33)	10
ZrL^3Cl_2	Red	79	195	30.07 (49.23)	3.78 (4.10)	6.27 (10.44)	17

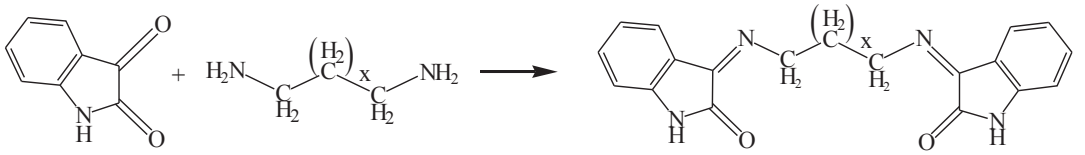
Calculated values are given in the parenthesis.

non-electrolytic character (Uddin *et al.* 2012). This revealed that all ligands were covalently bonded with zirconium.

FT-IR Spectra

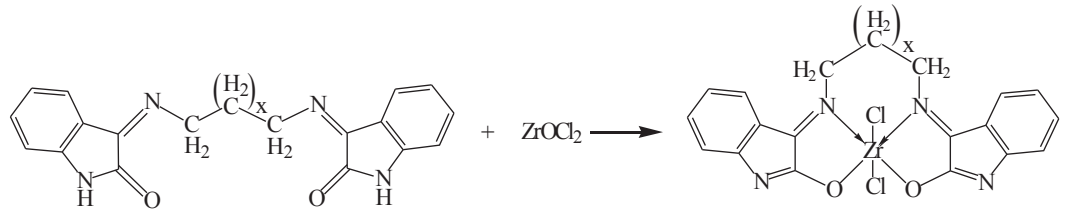
The infrared studies help to demonstrate the functional groups of the ligands and bonded in the complexes. FTIR spectra of the prepared N, N′-bis(isatin) diamine Schiff base iigands and their zirconium (IV) complexes are shown in Fig. 1 and 2, respectively. The spectra of the ligands should contain stretching bands for the azomethine group ((>C=N- group), C-N and C=O bonds at 1625-1582 cm^{-1} (Singh *et al.,* 2012), 1020-1250 cm^{-1} (Uddin *et al.,* 2012) and 1730-1750 cm^{-1} (Konstantinovic *et al.,* 2015) regions, respectively. The vibrational frequency at 3150-3300 cm^{-1} (Ade *et al.,* 2012) and 1460 cm^{-1} (Konstantinović *et al.,* 2015) correspond stretching and bending vibration of N-H bond. The broad IR band at 3400-3500 cm^{-1} (Ade *et al.,* 2012; Legzdins *et al.*,1989) arises due to the stretching vibration of O-H in water molecule. In the present experiment, we observed vibrational band at 1608-1610 cm^{-1} for the synthesized N, N′-bis (isatin) diamine ligands, which can be assigned for the azomethine group (>C=N-). This supports the formation of ligands through the condensation of isatin and diamine. The IR band at 1741-1751cm^{-1} refered to the stretching vibration in C=O bond of the ligands. The FT-IR band for stretching and bending vibration of N-H bond was observed at 3234-3267 cm^{-1} and 1463 cm^{-1}, respectively. The peak at 1203-1234 cm^{-1} indicated the presence of the C-N both in prepared ligands and complexes. The broad band observed at 3448- 3454 cm^{-1} relating to O-H stretching frequencies for moisture.

According to literature survey, ῡ (M-O) and ῡ (M-N) (where, M indicates metal) generally shows FT-IR band at 580-595 cm^{-1} and 430-460 cm^{-1} (Ade *et al*., 2012) respectively. The obtained FT-IR band at 650-750cm^{-1} and 447-472cm^{-1} indicated the presence of Zr-O and Zr-N bonds in complexes. The decrease of the sharpness of ῡC=O band (at 1732-1737cm^{-1}) as well as the disappearance of ῡN-H and δ N-H bands in the FT-IR spectra of complexes as compared to free ligand indicated that, on complexation the possible



Where x = 0, 1 and 4

Scheme A. Possible synthetic route of N, N′-bis (isatin) diamine ligand (L^n ; n =1, 2 and 3)



Where x = 0, 1 and 4

Scheme B. Possible synthetic route of N, N′-bis (isatin) diamino zirconium(IV) complex [ZrL^nCl_2] (n =1, 2 and 3).

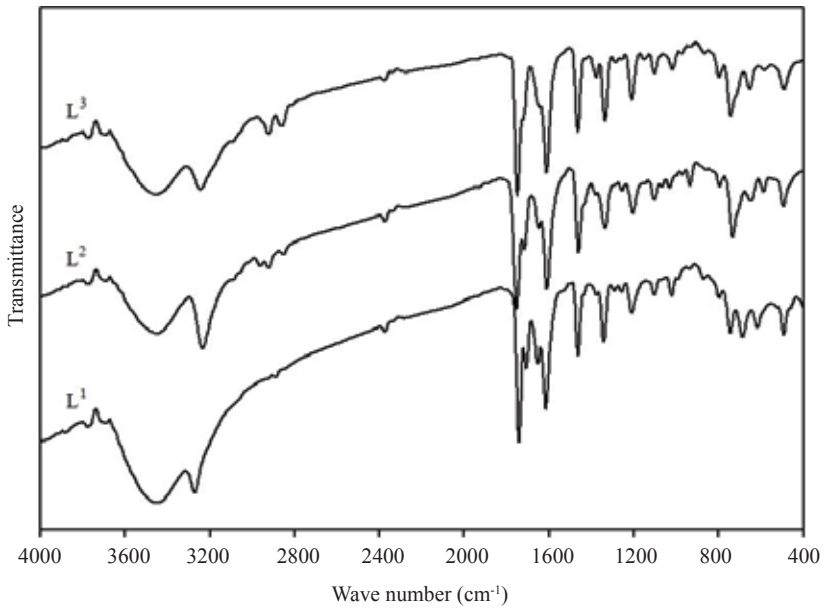


Fig. 1. FT-IR spectra of N, N′-bis (isatin) diamine ligands (L^n where n=1, 2 and 3)

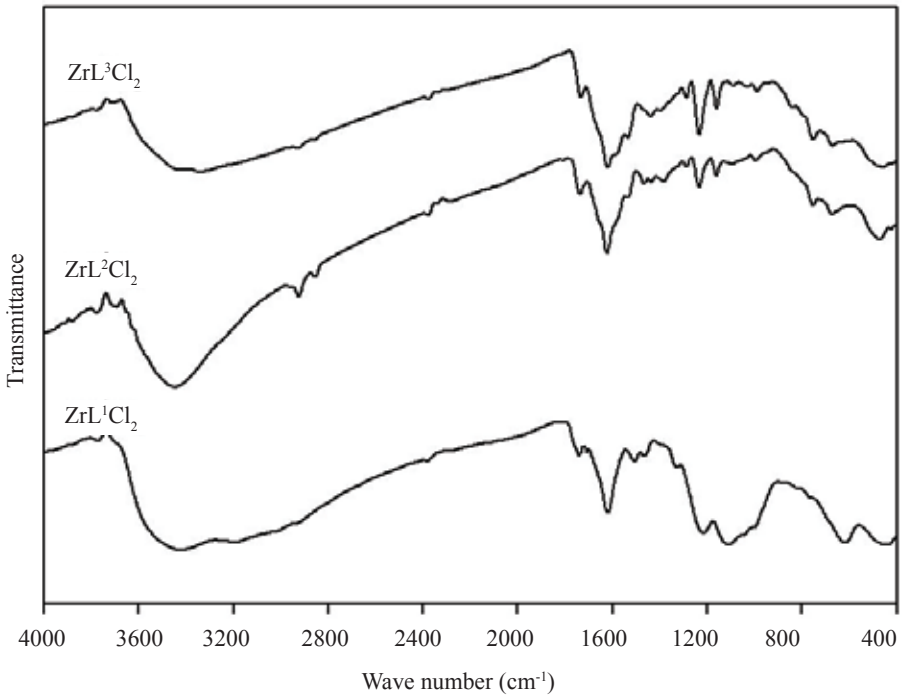


Fig. 2. FT-IR spectra of N, N′-bis (isatin) diamino zirconium(IV) complexes (ZrL^nCl_2 where, n= 1, 2 and 3)

deprotonation of N-H took place via the contiguous carbonyl oxygen in the isatin moiety through lactam-lactim tautomerism (Khalifa and Hassaan, 1995; Jiang *et al.,* 2017). The characteristic vibrational band of azomethine group (>C=N-) was observed at 1620-1624cm^{-1} in zirconium complex which was shifted to the higher frequency compared to ligand. This shifting can be explained due the participation of azomethine nitrogen in the coordination with Ziconium in the complex. Therefore, the FT-IR spectra of complexes support the formation of $[ZrL^nCl_2]$ complexes through the formation of coordination bonds with O, N donor. FT-IR spectral data for ligands and complexes are published in Table II and Table III, respectively.

^{1}H NMR Spectra

^{1}H NMR analysis of N, N′-bis (isatin)-1, 3-diaminopropane ligand (L^2) and N, N′-bis (isatin)-1, 3-diaminopropane zirconium(IV) complex $[ZrL^2Cl_2]$ were recorded using DMSO as solvent. ^{1}H NMR of the prepared ligand and complex are shown in Fig. 3 and 4, respectively. ^{1}H NMR spectral studies of Schiff base ligand usually give signals at δ = 6.47-7.67 ppm corresponding to aromatic protons (m, 7H, Ar-H) and at δ = 9.0 - 10ppm due to isatin moiety NH (Khalifa and Hassaan, 1995; Ade *et al.,* 2012). According to

Table II. Infrared spectral data of N, N′-bis (isatin) diamine Schiff base ligands

Ligands	ῡC=N cm^{-1}	ῡC-N cm^{-1}	ῡC=O cm^{-1}	δN-H cm^{-1}	ῡN-H cm^{-1}
L^1	1610.56	1203.58	1741.72	1463.97	3267.41
L^2	1608.63	1203.58	1751.36	1462.04	3234.62
L^3	1610.56	1209.37	1749.44	1463.97	3244.27

Table III. Infrared spectral data of N, N′-bis (isatin) diamino Zr(IV) complexes

Complexes	ῡC=N cm^{-1}	ῡC-N cm^{-1}	ῡC=O cm^{-1}	ῡZr-O cm^{-1}	ῡZr-N cm^{-1}
ZrL^1Cl_2	1620.21	1215.15	1735.93	614.34	447.49
ZrL^2Cl_2	1624.06	1234.44	1737.86	673.16	472.56
ZrL^3Cl_2	1620.21	1232.51	1732.06	671.23	459.06

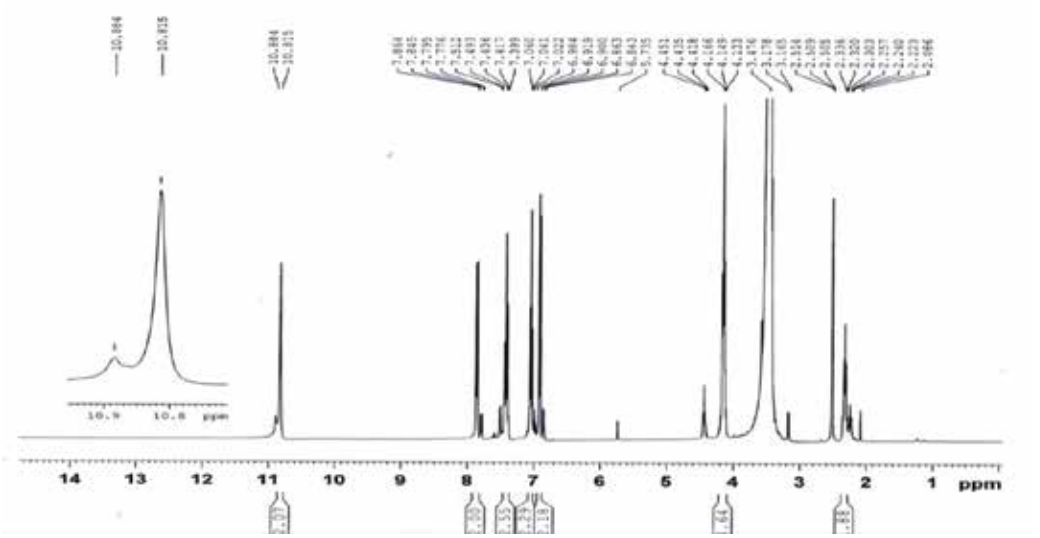


Fig. 3. ^{1}H NMR spectrum of N, N′-bis (isatin) 1, 3- propylenediamine ligand (L^2)

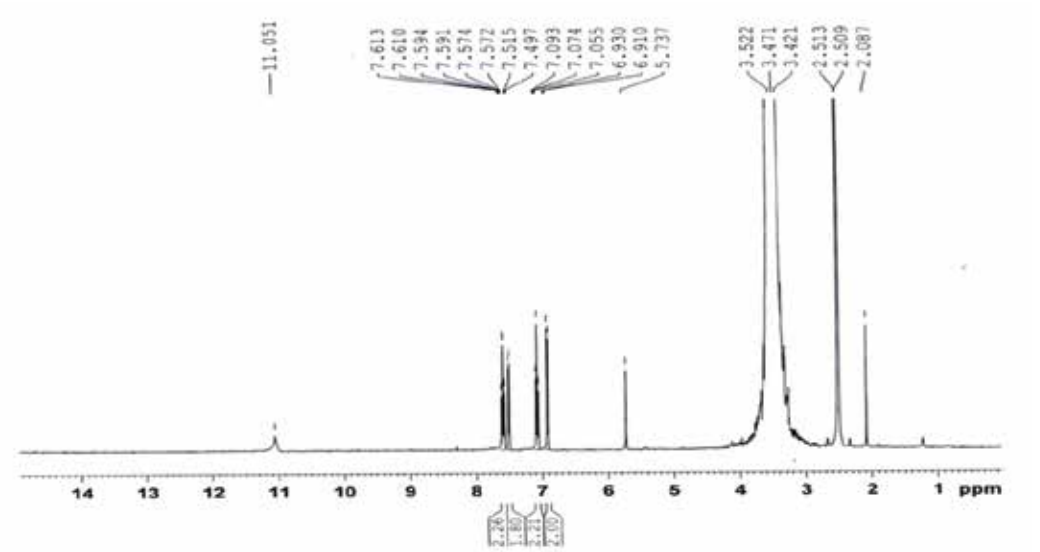


Fig. 4. ^{1}H NMR spectrum of zirconium complex of N, N′-bis (isatin)-1, 3-diaminopropane ligand [ZrL^2Cl_2]

the proposed structure of selective ligand and complex, there are two types of $–CH_2$ groups in both ligand and complex that comes from the diamine. First one is two terminal $–CH_2$ and second one is middle $–CH_2$ group. For middle $–CH_2$ group multiplate was obtained at δ = 2.240-2.336 ppm with the integrated value 1.8 and the terminal $-CH_2$ protons assigned from triplet at the range δ= 4.133- 4.166 ppm. There are two terminals $–CH_2$ group in the ligand therefore, the integrated value for these protons was 4.64. The presence of these peaks proves that the aliphatic chain is present in the ligand that bridges two isatin moiety and support the formation of ligand. The phenyl protons were observed at the chemical shift δ=6.863- 7.864 ppm for ligand and in δ= 6.910-7.613 for the complex. The obtained integrated values of protons on phenyl part for ligand were 2.18, 2.29, 2.55 and 2.00 and that for complex were 2.00, 2.21, 2.80 and 2.26, respectively which indicate the presence of two phenyl groups in both the ligand and complex. The peaks for these two phenyl groups with eight integrated protons in the complex as like as ligand indicate the existence of ligand in the complex. The peak obtained in δ= 10.815- 10.884 ppm for ligand was assigned for NH proton of isatin moiety. The N-H protonic peak in the complex gets almost disappeared through downfield shifting to δ= 11.051 ppm with respect to the ligand and indicated the lactam-lactim equilibrium (Khalifa and Hassaan, 1995; Jiang *et al.* 2017). Therefore, the ^1H NMR also support the FT-IR result.

Electronic spectra

The N, N′-bis (isatin) diamine ligands and their Zr (IV) complexes are soluble in DMSO and DMF but insoluble in methanol, ethanol, and CCl_4. Therefore, the electronic spectra of Schiff bases and its zirconium complexes were recorded in DMF. The UV spectra of the ligands and their complexes are shown in the Fig. 5 and 6, respectively. The electronic spectra of Schiff base ligand exhibit bands at 230, 290 due to π-π* transition and 380 nm n-π* transitions (Kriza and Parnau, 2001). In the UV spectra of ligands, bands at 240, 260 and 295 nm can be assigned due to the π-π*

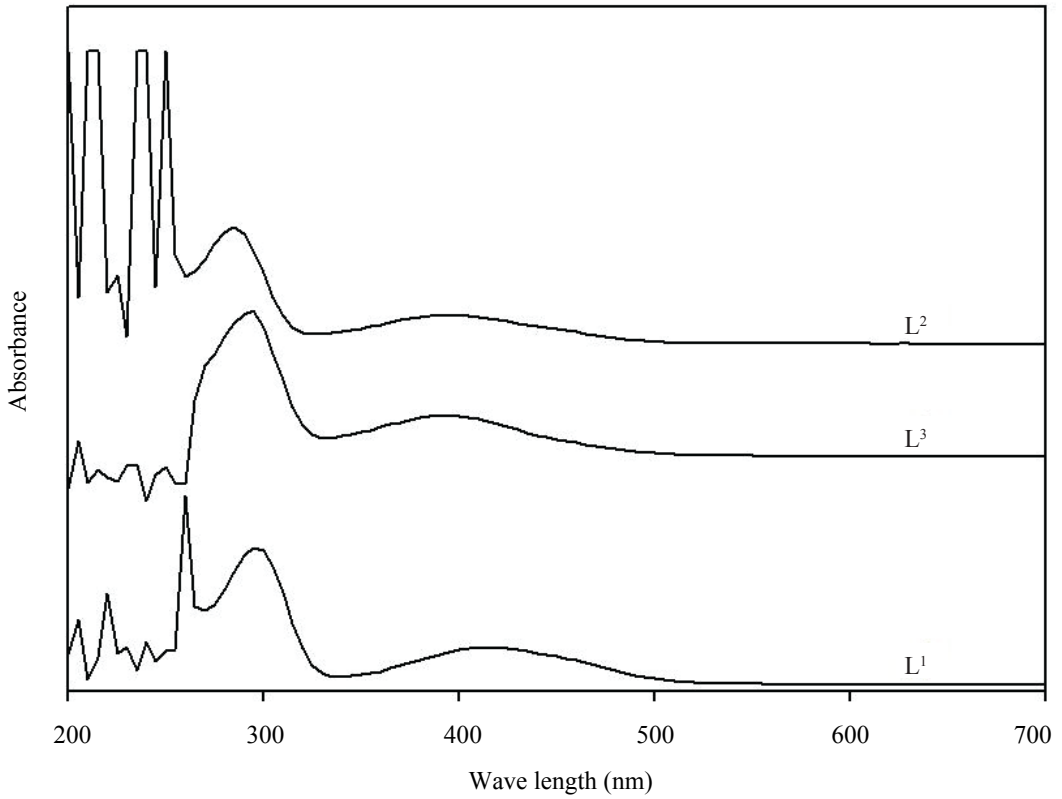


Fig. 5. UV-visible spectra of N, N′-bis (isatin) diamine ligands

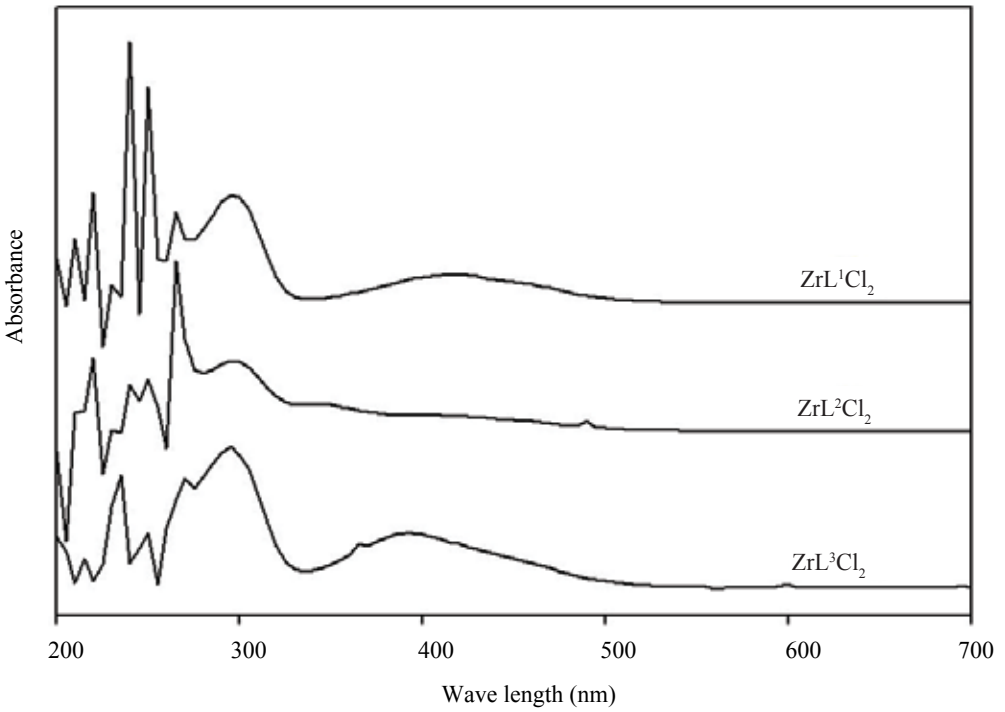


Fig. 6. UV-visible Spectra of N, N′-bis (isatin) diamino zirconium (IV) complexes

Table IV. Electronic spectral data for the N, N′-bis (isatin) diamino ligands.

Ligands	Medium	Electronic spectral bands in (nm)
L^1	DMF	220, 240, 260, 295, 415
L^2	DMF	221, 235, 250, 285, 395
L^3	DMF	220, 250, 290, 385

Table V. Electronic spectral data of N, N′-bis (isatin) diamino zirconium (IV) complexes

Ligands	Medium	Electronic spectral bands in (nm)
ZrL^1Cl_2	DMF	240, 250, 265, 295, 395
ZrL^2Cl_2	DMF	270, 295
ZrL^3Cl_2	DMF	235, 250, 270, 295, 395

transitions within the aromatic ring which remain almost unchanged in the spectra of zirconium complexes. Another band at 385-415 nm is due to the n-π* transitions within the >C=N- group. The d-d electronic transition generally shows band around 550nm but pure d-d origin are not expected in the zirconium (IV) complexes having $4d^0$ configuration (Jafarpour *et al.,* 2013). In the UV spectra of present complexes, there was no absorption band found beyond 500 nm. This revealed the absence of d-d electronic transition over the visible region. Thus the electronic spectral data clearly confirmed that the complexes are genuine zirconium (IV). The complexes are, however, colored only through their absorptions tailing in the form of ultraviolet. Electronic spectral data are shown in Table IV and V for the prepared complexes.

Conclusion

The N, N′-bis (isatin) diamino Schiff base ligands were prepared by the usual condensation of isatin and diamine like ethane-1, 2-diamine, propane-1,3-diamine and hexane-1,6-diamine in 1:2 molar ratio. Zirconium complexes of these prepared ligands were synthesized by the reaction of the ligands and zirconium (IV) oxychloride octahydrate ($ZrOCl_2.8H_2O$). The prepared ligand and complexes were found to be of the type L^n and ZrL^nCl_2 (where, n = 1, 2, 3). The analytical data indicated that the complexes have 1:1 (metal:ligand) stoichiometry. Molar conductance value indicated the non-electrolytic nature of the prepared complexes. Azomethine ῡC=N band in the FT-IR spectra indicating the successful formation of ligands. The shifting of ῡC=N band to the higher frequency in complexes indicated the influence of coordination of ligand with zirconium. The disappearance of ῡN-H and δN-H bands and de-intensification of ῡC=O indicated the lactam-lactim equilibrium. The appearance of ῡZr-O and ῡZr←N modes indicated the formation of metal-ligand coordination compound In ^{1}H NMR spectra the peaks for eight integrated protons of two phenyl groups and protons for methylene groups of bridging diamines in both the ligands and complexes pointed out their existence. The peak for NH proton at δ= 10.815- 10.884 ppm of ligand gets almost disappeared in the complex indicated deprotonation through tautomerism due to the formation of coordinate bond and support the FTIR result. In the electronic spectra we observed absorption bands in the range below 500 nm. The absence of peak above 500 nm suggested that there is no electron in the d orbital of zirconium metal. It reveled the formation of complexes where zirconium exists in +4 oxidation state. The elemental analysis showed good agreement of experimental and theoretical percentage of C, H, and N in both ligands and their complexes. On the basis of overall analysis in this research, the formation of N, N′-bis (isatin) diamino zirconium (IV) complex (ZrL^nCl_2) with octahedral geometry could be expected. However, without crystal structure determination, it is difficult to put forward the exact geometry of ZrL^nCl_2 complexes. Therefore, further study is required to illustrate the precise structure of the prepared complexes and the mode of reaction.

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