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SOME RUTHENIUM (II) COMPLEXES WITH NEW MACROCYCLIC LIGANDS: A PHOTOELECTRON STUDY

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ABSTRACT

Ten complexes of the type $[\text{RuCl}_2\text{L}^{1-10}]$ (Where L = macrocyclic Schiff base ligands; derived from condensation of thiodiglycolic acid and different aliphatic diamines) have been synthesized by reaction of $[\text{RuCl}_2(\text{DMSO})_4]$. These complexes were characterized by elemental analysis, molar conductance, UV-visible spectra, IR, magnetic moment and X-ray photoelectron (XPS) spectra. An octahedral geometry was also established for all these complexes.

INTRODUCTION

The macrocyclic ligands and their metal complexes have been extensively studied in last few decades due to macrocyclic ligands utilization in coordination chemistry[1-7]; catalysis[8-14]; bioinorganic chemistry[15-16]; organometallic chemistry[17] and biocoordination[18]. Many macrocyclic Schiff base ligands have also been synthesised by the template condensation reactions[19-21]. Many different types of macrocyclic ligands have also been synthesized e.g. N_4S_2 donor macrocyclic ligands [22-29]; crown ethers[30]; porphyrins[8]; saturated and unsaturated polyamines [22-28,31-47]; polyazamacrocycles[43,48-51] and Robson type tetraaminodiphenol macrocyclic ligands [31,35-36, 41, 44-46].

Macrocyclic metal complexes have also been used as anticancerous[52]; as in metal ion separation[13,53-54]; as in detecting tumor lesions[55]; as toxicity against bacterial fungal growth[56]; as photosensitizer[57-58]; as catalyst[59-62]; as in photosynthesis and dioxygen transport[63-64], as in pharmacological agent[65-67]; as cancer diagnosis[62,68-69]; as therapeutic, radiotherapeutic[70-71]; as antitumour[72]; as medicinal applications[68,73]; as environmental applications[74]; as RNA cleavage catalyst[75-76], and as NMR shift and relaxation agents[77-78]. Recently six reviews have also been published

which covers about ruthenium metal complexes and their applications with different macrocyclic ligands[79-84].

The literature survey of last few decades revealed that although many ruthenium (II) and ruthenium (III) metal complexes with different macrocyclic ligands have been synthesized and characterized; ruthenium (II) metal complexes are less reported [29,85-94]. In this present research paper ten new macrocyclic ligands have been synthesized (which are derived from thiodiglycolic acid and different aliphatic diamines) and by interaction of each these ligand with $[\text{RuCl}_2(\text{DMSO})_4]$; new ruthenium (II) metal complexes of the type $[\text{RuCl}_2\text{L}^{1-10}]$ have been synthesized and characterized.

EXPERIMENTAL

The chemicals thiodiglycolic acid (Aldrich); $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (Johnson Matthey & Co. Ltd.); Dimethylsulphoxide i.e. DMSO (Aldrich); $\text{NH}_2(\text{CH}_2)_2\text{NH}_2$ (BDH); $\text{NH}_2(\text{CH}_2)_3\text{NH}_2$ (BDH); $\text{NH}_2(\text{CH}_2)_4\text{NH}_2$ (BDH); $\text{NH}_2(\text{CH}_2)_5\text{NH}_2$ (BDH); $\text{NH}_2(\text{CH}_2)_6\text{NH}_2$ (BDH); $\text{NH}_2(\text{CH}_2)_7\text{NH}_2$ (BDH); $\text{NH}_2(\text{CH}_2)_8\text{NH}_2$ (BDH); $\text{NH}_2(\text{CH}_2)_9\text{NH}_2$ (BDH); $\text{NH}_2(\text{CH}_2)_{10}\text{NH}_2$ (BDH); CH_3COCH_3 (Aldrich); CH_3OH (BDH) and DMF (Aldrich) were AR Grade and used after purification and dried as given in literature[95-96]. $[\text{RuCl}_2(\text{DMSO})_4]$ was synthesized by the method given in the literature[97]. Melting points were measured by using capillary tubes on Buchi-SMP-20 capillary Melting Point Apparatus. Chlorine and nitrogen were determined by Volhard's and Kjeldahl's methods respectively[95-96]. The C and H percentage elemental analysis were done by CDRI, Lucknow, India. Molar conductance were measured by Elico CM 8.2 Conductivity Bridge at room temperature in DMF. IR spectra were recorded on Perkin-Elmer 1000 IR spectrometer using CsI pellets. Electronic spectral measurements were recorded on Elico SL159 spectrophotometer in the range 300-1000 nm using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant. Magnetic measurements were carried out on a Cahn 2000 electrobalance by Faraday Method. X-ray photoelectron spectra (XPS) were recorded on VG Scientific ESCA-II spectrometer using $\text{AlK}\alpha$ (1486.6 eV) as source. All photoelectron peaks were corrected for charging with reference to C1s peak 284.8 eV and fitted with Shirley background and a combination of Gaussian and Lorentzian line-shapes using Escape software [98-99].

Preparation of $[\text{RuCl}_2\text{L}^{1-10}]$ Complexes:

(2 mmol) thiodiglycolic acid was mixed in dry methanol solution of (2 mmol) $\text{NH}_2(\text{CH}_2)_n\text{NH}_2$ (where $n=2$ or 3 or 4 or 5 or 6 or 7 or 8 or 9 or 10 or 12) in dry methanol solvent and refluxed for two hours. In each resulting solution $[\text{RuCl}_2(\text{DMSO})_4]$, poured (1 mmol) and again refluxed for 2 hours. The resulting precipitate was filtered and recrystallized by benzene, pet-ether (9:1) ratio (Fig. 1).

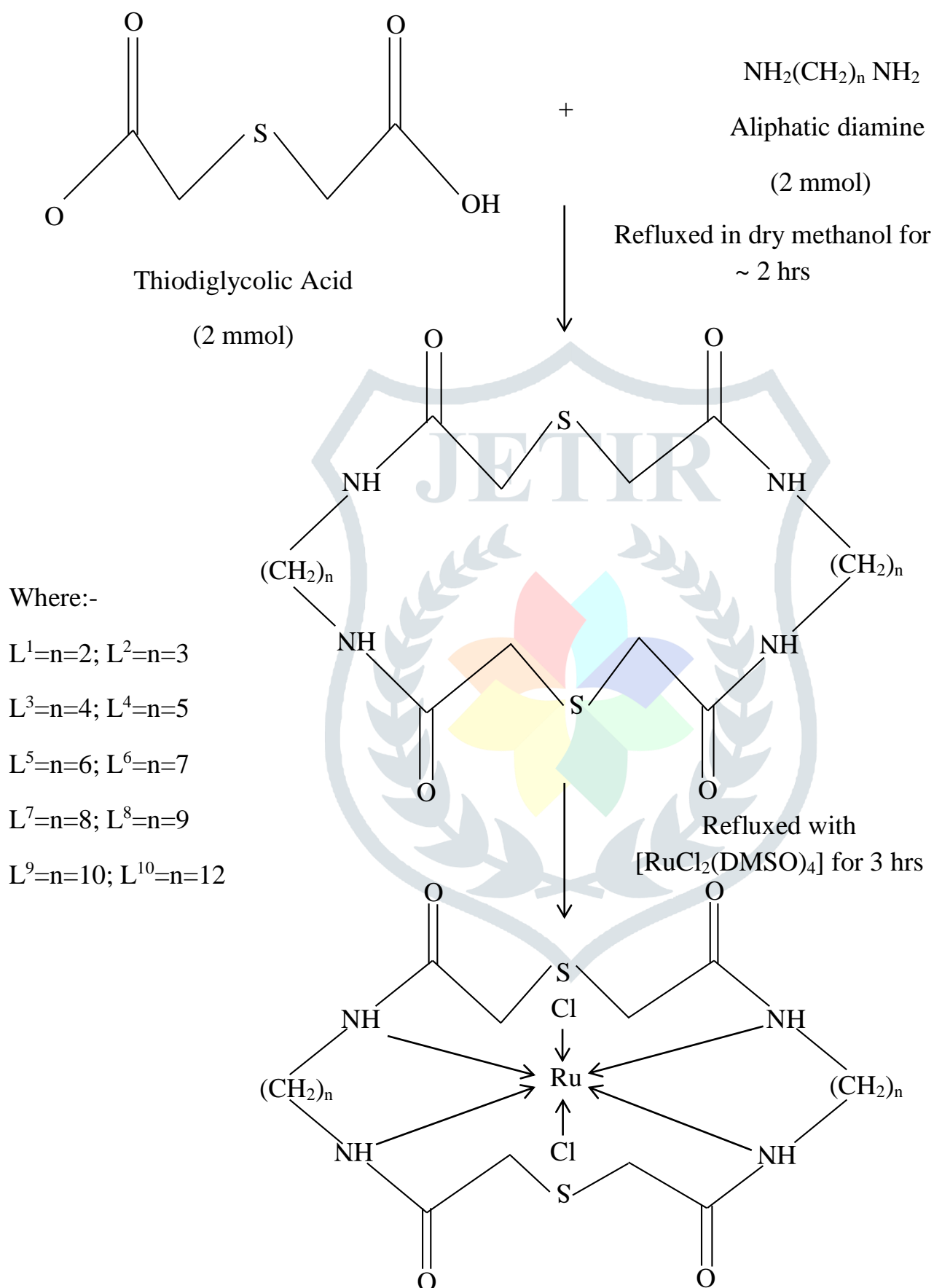
Fig. 1 – Preparation of $[\text{RuCl}_2 L^{1-10}]$ complexes

Table I : Ru3p_{1/2}, 3/2; N1s; O1s; S2p_{1/2}, 3/2 and Cl2p binding energies (eV) in Ligands; [RuCl₂(DMSO)₄] and [RuCl₂L¹⁻¹⁰] metal complexes

Sr. No.	Ligand & Complex	Ru3p _{1/2} , 3/2		N1S		O1s	S2p _{1/2} , 3/2
		Ru3p _{1/2}	Ru3p _{3/2}	Uncoord.	Coord.		
1	L ¹	-	-	400.8	-	531.0	166.0
2	L ²	-	-	400.8	-	531.0	166.0
3	L ³	-	-	400.8	-	531.0	166.0
4	L ⁴	-	-	400.8	-	531.0	166.0
5	L ⁵	-	-	400.8	-	531.0	166.0
6	L ⁶	-	-	400.8	-	531.0	166.0
7	L ⁷	-	-	400.8	-	531.0	166.0
8	L ⁸	-	-	400.8	-	531.0	166.0
9	L ⁹	-	-	400.8	-	531.0	166.0
10	L ¹⁰	-	-	400.8	-	531.0	166.0

Sr. No.	Ligand & Complex	Ru3p _{1/2} , 3/2		N1S		O1s	Cl2p	S2p _{1/2} , 3/2
		Ru3p _{1/2}	Ru3p _{3/2}	Uncoord.	Coord.			
11	RuCl ₂ (DMSO) ₄	482.2	460.2	-	-	531.0	201.4	166.8
12	[RuCl ₂ L ¹]	481.0	459.0	-	402.4	531.0	202.8	166.0
13	[RuCl ₂ L ²]	481.0	459.0	-	402.4	531.0	202.8	166.0
14	[RuCl ₂ L ³]	481.0	459.0	-	402.4	531.0	202.8	166.0
15	[RuCl ₂ L ⁴]	481.0	459.0	-	402.4	531.0	202.8	166.0
16	[RuCl ₂ L ⁵]	481.0	459.0	-	402.4	531.0	202.8	166.0
17	[RuCl ₂ L ⁶]	481.0	459.0	-	402.4	531.0	202.8	166.0
18	[RuCl ₂ L ⁷]	481.0	459.0	-	402.4	531.0	202.8	166.0
19	[RuCl ₂ L ⁸]	481.0	459.0	-	402.4	531.0	202.8	166.0
20	[RuCl ₂ L ⁹]	481.0	459.0	-	402.4	531.0	202.8	166.0
21	[RuCl ₂ L ¹⁰]	481.0	459.0	-	402.4	531.0	202.8	166.0

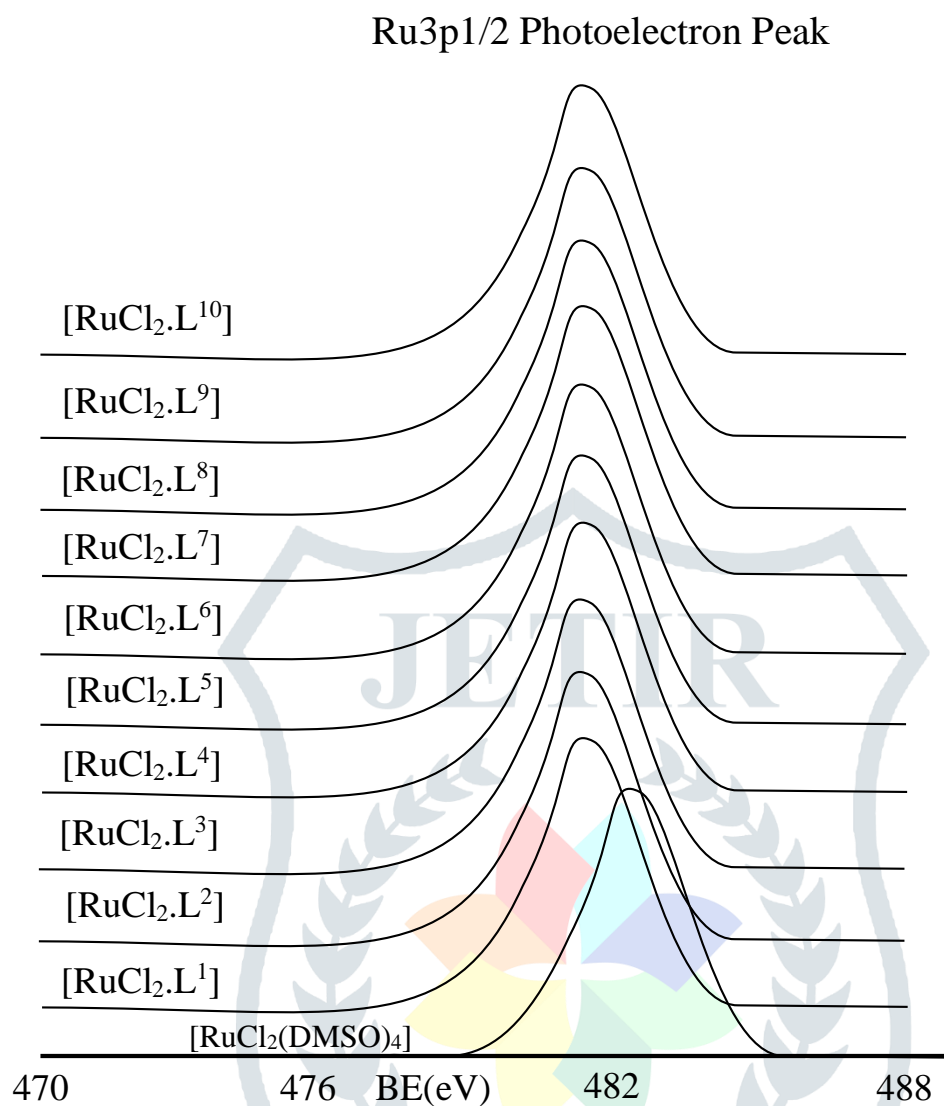


Fig. 2 : Ru3p1/2 binding energies (eV) in $[\text{RuCl}_2(\text{DMSO})_4]$ and $[\text{RuCl}_2\text{L}^{1-10}]$ complexes

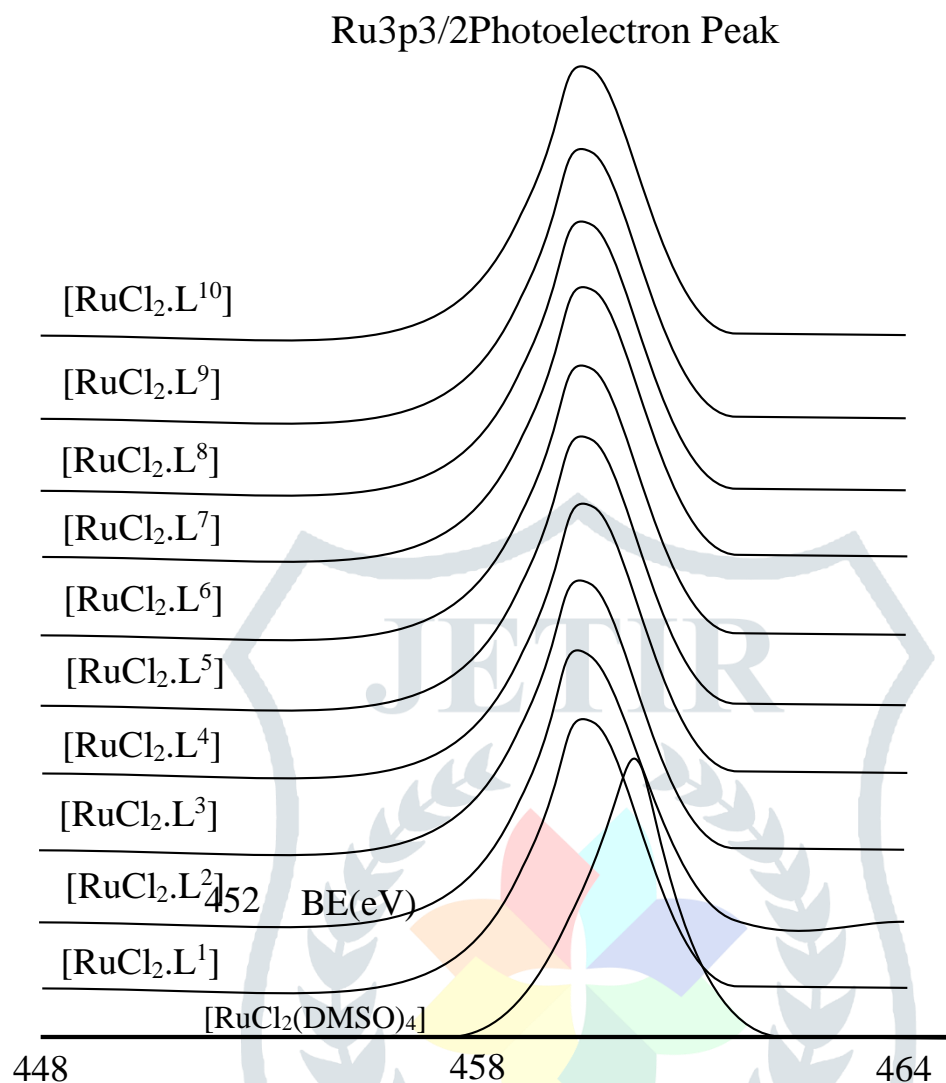


Fig. 3 : Ru3p3/2 binding energies (eV) in [RuCl₂(DMSO)₄] and [RuCl₂L¹⁻¹⁰] metal complexes

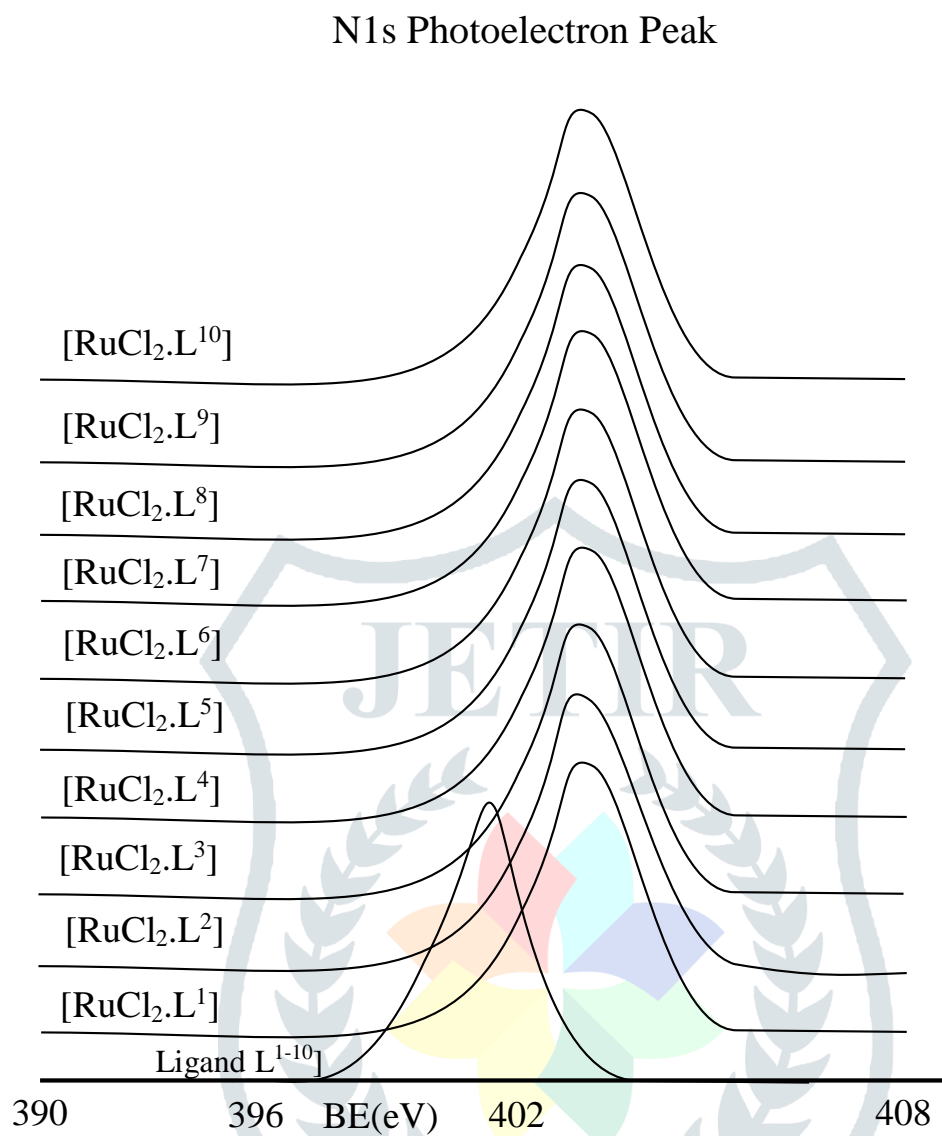


Fig. 4 : N1s binding energies (eV) in ligands and $[RuCl_2L^{1-10}]$ complexes

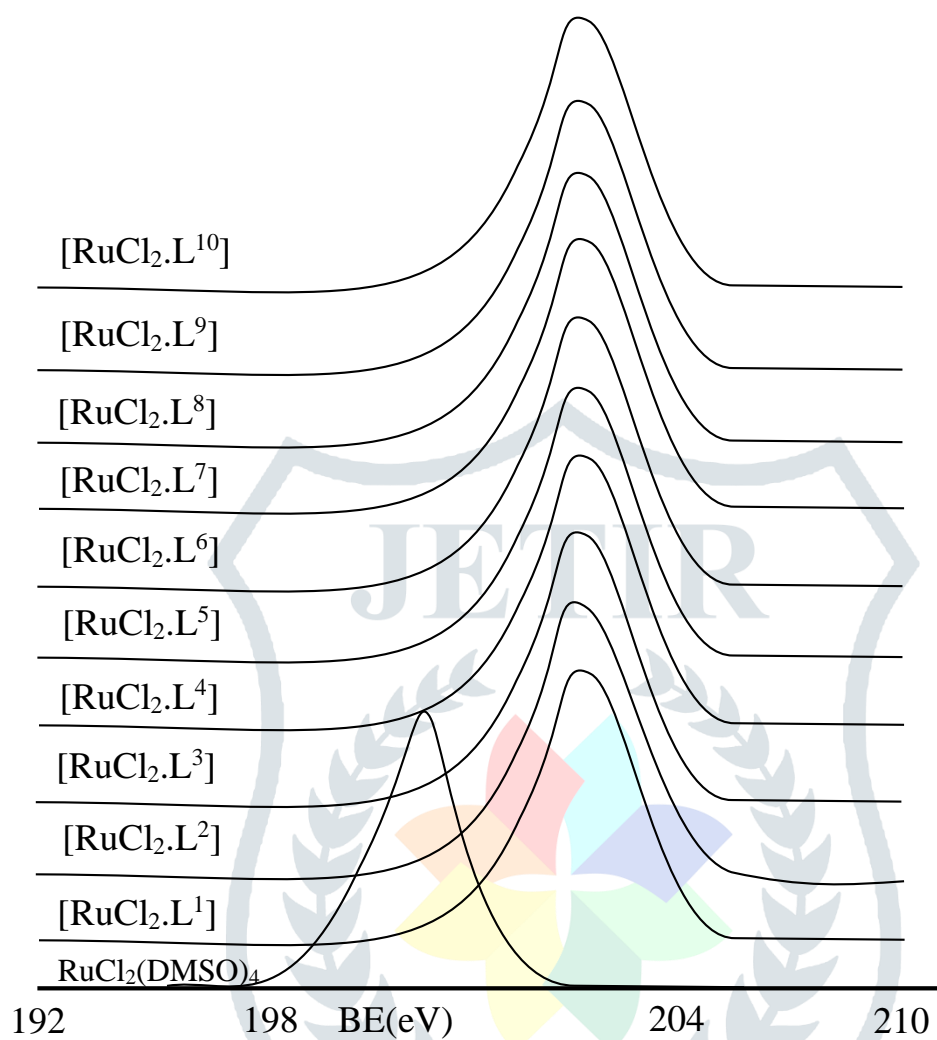
Cl₂p_{1/2}, 3/2 Photoelectron Peak

Fig. 5 : Cl₂p binding energies (eV) in $[\text{RuCl}_2(\text{DMSO})_4]$ and $[\text{RuCl}_2\text{L}^{1-10}]$ complexes

S2p1/2, 3/2 Photoelectron Peak

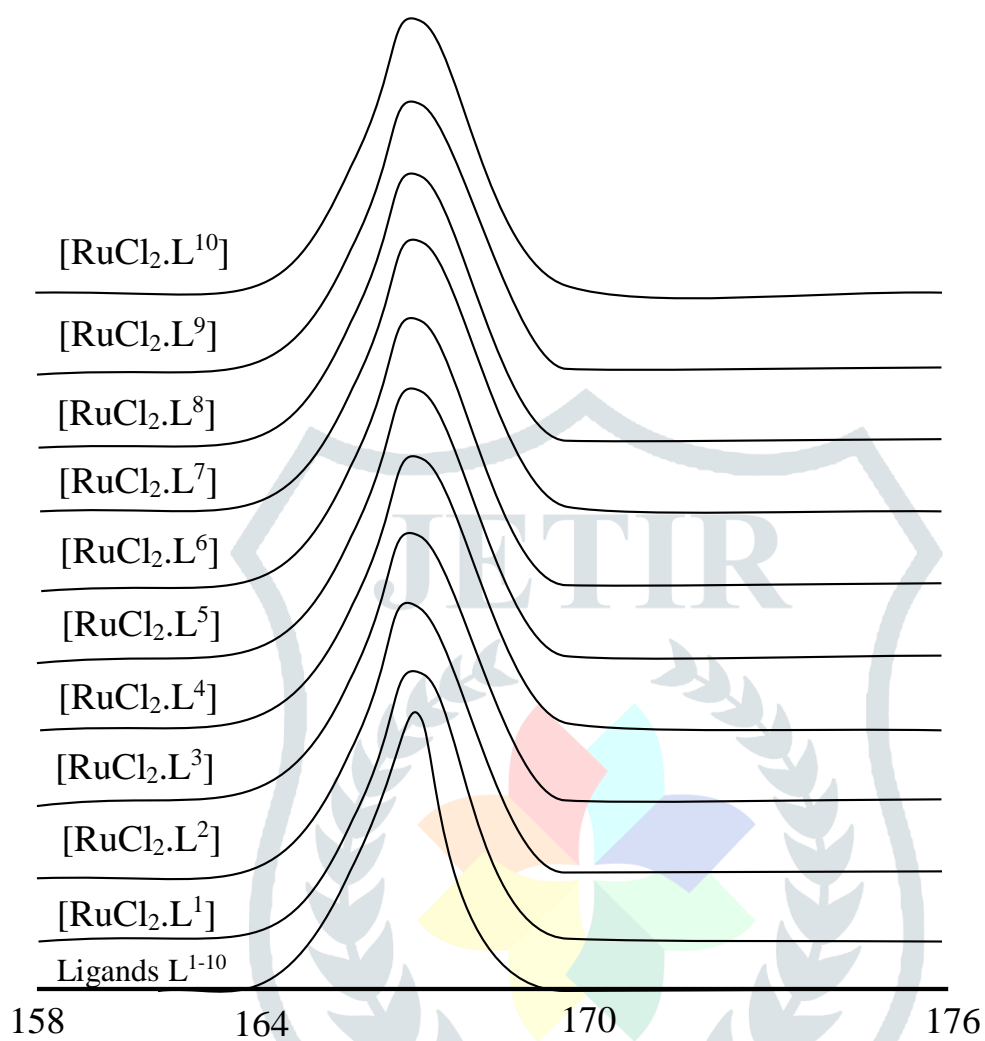


Fig. 6 : S2p1/2, 3/2 binding energies (eV) in ligands and [RuCl₂L¹⁻¹⁰] complexes

O1s Photoelectron Peak

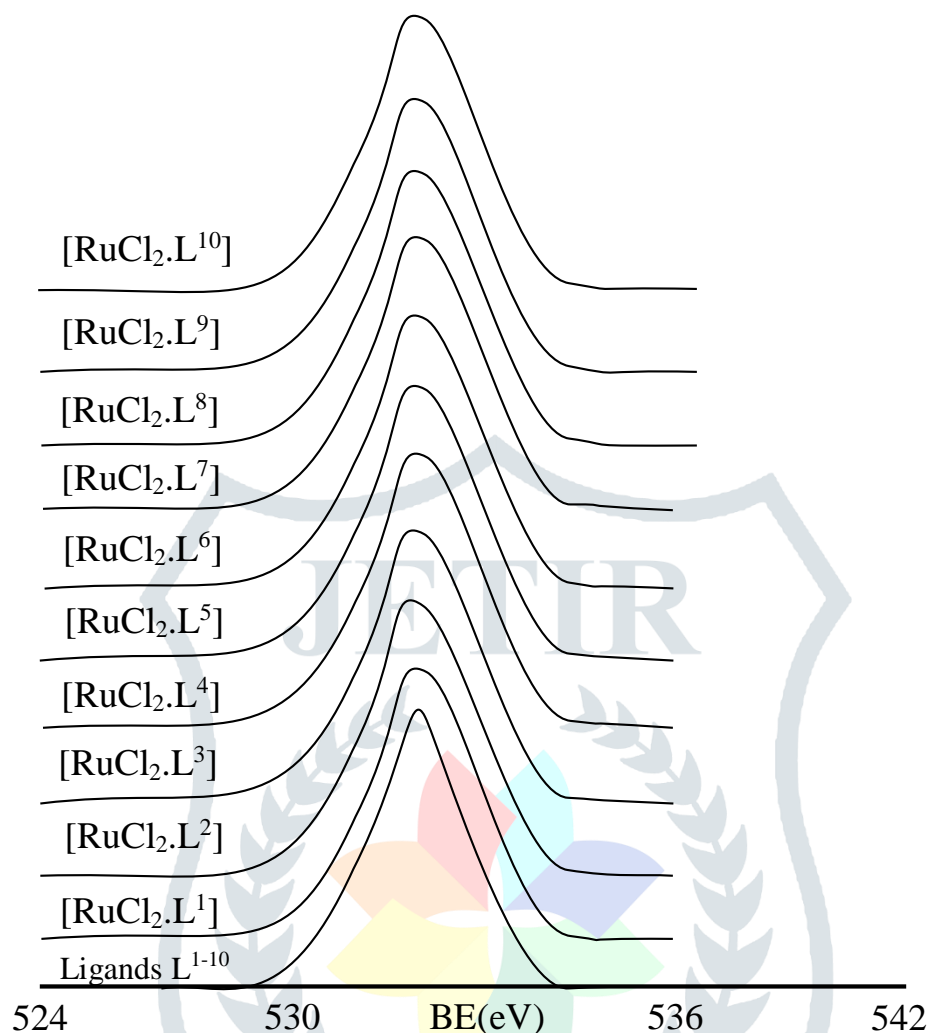


Fig. 7 : O1s binding energies (eV) in ligands and $[\text{RuCl}_2\text{L}^{1-10}]$ complexes

RESULTS AND DISCUSSION

Ten Ru (II) complexes with N_4S_2 macrocyclic ligands were prepared by interaction of each N_4S_2 macrocyclic ligand with $[\text{RuCl}_2(\text{DMSO})_4]$; in which each macrocyclic were derived from condensation of thiodiglycolic acid (2 mmol) with different aliphatic diamine (2 mmol) in dry methanol solvent. The calculated and found percentage of C, H, N and Cl elemental analysis were found within $\pm 0.5\%$. The molar conductance in each complex was obtained below $12\text{-}30 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ suggesting nonelectrolyte nature and proposed structure composition as $[\text{RuCl}_2\text{L}^{1-10}]$ [101]. In each complex IR band due to $\nu\text{C}=\text{N}$ was shifted towards lower side band $20\text{-}40 \text{ cm}^{-1}$ with respect to the ligand band and was obtained in the range of $1600\text{-}1550 \text{ cm}^{-1}$ [77]. A low intensity band have also shown in the range of $520\text{-}500 \text{ cm}^{-1}$ due to $\nu\text{Ru-N}$ vibration suggested that ligand is coordinated to Ruthenium metal ion through nitrogen of $\text{C}=\text{N}$ group in each prepared complex. One IR band was also observed in the range of $320\text{-}300 \text{ cm}^{-1}$, suggesting presence of two chlorine ions in trans position around ruthenium ion[102]. Each $[\text{RuCl}_2\text{L}^{1-10}]$ complex have also shown characteristic IR bands of aromatic ring in the expected region[102]. In each $[\text{RuCl}_2\text{L}^{1-10}]$ complex, four electronic transition bands were shown due to $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$; $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$; $^1\text{A}_{1g} \rightarrow ^3\text{T}_{2g}$; $^1\text{A}_{1g} \rightarrow ^3\text{T}_{1g}$; suggesting octahedral geometry. Two electronic bands were shown in the region $200\text{-}530 \text{ nm}$ due to the spin allowed $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ transition at lower

wavelength[103]. Another high intensity band were shown at 280-290 nm region due to charge transfer from the excitation of an electron from the metal t_{2g} level to the unfilled molecular orbital derived from the π^* level of ligands[103]. The negative value of magnetic susceptibility in each $[\text{RuCl}_2\text{L}^{1-10}]$ complex at room temperature suggested diamagnetic nature of each complex.

For $\text{Ru}3p_{1/2}$, $3/2$; $\text{N}1s$; $\text{Cl}2p$; $\text{O}1s$ and $\text{S}2p$ photoelectron peaks binding energies (eV) values for ten prepared ligands i.e. L^{1-10} ; $[\text{RuCl}_2(\text{DMSO})_4]$ and prepared complexes $[\text{RuCl}_2\text{L}^{1-10}]$ are listed in Table 1 (Fig. 2 to 7). It was observed that $\text{Ru}3p_{1/2}$ and $\text{Ru}3p_{3/2}$ binding energies (eV) were higher in starting material $[\text{RuCl}_2(\text{DMSO})_4]$ ($\text{Ru}3p_{1/2}$ BE= ~ 482.2 eV and $\text{Ru}3p_{3/2}$ BE = ~ 460.2 eV) than in prepared $[\text{RuCl}_2\text{L}^{1-10}]$ complex ($\text{Ru}3p_{1/2}$ BE= ~ 481.0 eV and $\text{Ru}3p_{3/2}$ BE= 459.0 eV); suggested that coordination electron density is more in each metal complex $[\text{RuCl}_2\text{L}^{1-10}]$ on ruthenium metal ion[99-100]. In each $[\text{RuCl}_2\text{L}^{1-10}]$ metal complex, only one single symmetrical $\text{N}1s$ photoelectron peak was observed at higher binding energy side than each $\text{N}1s$ photoelectron binding energy of each ligand, suggested all four nitrogen atoms are coordinated with ruthenium metal ion[99-100]. One sharp photoelectron peak at BE= ~ 202.8 have also shown in each $[\text{RuCl}_2\text{L}^{1-10}]$ complex, which was higher binding energy side than $\text{Cl}2p$ binding energy ($\text{Cl}2p$ BE= 201.4 eV) of $[\text{RuCl}_2(\text{DMSO})_4]$; suggested both chlorine atoms in each $[\text{RuCl}_2\text{L}^{1-10}]$ are coordinated and in trans position with inner sphere chlorine atom[99-100]. The $\text{O}1s$ and $\text{S}2p_{1/2,3/2}$ binding energies (eV) in each complex $[\text{RuCl}_2\text{L}^{1-10}]$ were observed in same position as in each ligand ($\text{O}1s$ BE= 531.0 eV and $\text{S}2p$ BE= 166.0 eV); suggest non-involvement of oxygen and sulphur atoms in coordination in each $[\text{RuCl}_2\text{L}^{1-10}]$ complex. The $\text{Ru}3s_{1/2}$ photoelectron peak in each $[\text{RuCl}_2\text{L}^{1-10}]$ complex, have shown one single photoelectron peak without splitting or asymmetric nature suggesting diamagnetic nature of each complex[99-100].

CONCLUSION

On the basis of elemental analysis; molar conductance; electronic spectra; IR; magnetic susceptibility and X-ray photoelectron spectra (XPS); the structure of each prepared complex may be assigned as $[\text{RuCl}_2\text{L}^{1-10}]$ as shown in Fig. 1 and an octahedral geometry may be established for each complex.

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