



## Synthesis and Spectral Studies of Ru(II) complexes with Macrocyclic Ligands

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### ABSTRACT

Fifteen Ru(II) complexes of the type  $[\text{RuCl}_2(\text{L})_2]$  (where  $\text{L}=\text{N}_4$  donor macrocyclic ligands) have been synthesised by reaction of  $[(\text{RuCl}_2(\text{DMSO})_2)_2]$  with fifteen macrocyclic Schiff base ligands containing  $\text{N}_4$  donors groups. The prepared fifteen  $[\text{RuCl}_2(\text{L})_2]$  complexes were characterised by elemental analyses, molar conductivity, UV-Visible, IR, X-ray photoelectron spectra (XPS) and magnetic susceptibility measurements and an octahedral geometry was proposed for all these complexes.

**Keywords:**  $\text{N}_4$  macrocyclic Schiff base complexes, Ru(II) complexes, elemental analysis, UV-Visible, Magnetic susceptibility measurement, X-ray photoelectron spectra (XPS).

### INTRODUCTION

During past few decades the chemistry of macrocyclic of metal have been developed very extensively due to its applications in coordination chemistry<sup>1,2</sup>; bioinorganic chemistry<sup>3</sup> catalysis<sup>4-6</sup>; organometallic chemistry<sup>7</sup> and biocoordination chemistry<sup>8</sup>. Many macrocyclic ligands e.g. Robson type tetraaminodiphenol macrocyclic ligands<sup>9,10</sup>;  $\text{N}_4\text{S}_2$  donor macrocyclic ligands<sup>11</sup>; crown ethers; porphyrins; saturated and unsaturated polyamine<sup>6-12</sup>; polyazamacrocycles<sup>18</sup>; have been synthesised.

A number of Schiff base macrocyclic ligands have been reported<sup>14</sup>. In which many macrocyclic ligands have been synthesised by the template condensation reaction<sup>15</sup>. Several transition metal ion complexes in living organisms work as enzymes or carriers in macrocyclic ligand environment<sup>16</sup> and used as modelling on the active sites of metalloenzymes<sup>17</sup>.

Various macrocyclic metal complexes have been used as detecting tumor lesions<sup>18</sup> as in labeling monoclonal antibodies with radioactive models<sup>19</sup> as in



metal ion separation<sup>20</sup> as anticancerous<sup>21</sup> as toxicity against bacterial fungal growth<sup>22</sup> as photosensitizer<sup>23</sup>; in photosynthesis and dioxygen transport<sup>24</sup>; catalyst<sup>25-27</sup> as pharmacological agent;<sup>28,29</sup> cancer diagnosis<sup>30-32</sup> as therapeutic radiotherapeutic<sup>33</sup> as antitumour<sup>34</sup> as potential medical applications<sup>35</sup> as environmental importance<sup>36</sup> as RNA cleavage catalyst<sup>37</sup> and as NMR shift and relaxation agents<sup>38</sup>.

Few comprehensive reviews on macrocyclic ligands, their metal complexes and applications have been also published in last few years<sup>39</sup>.

Many ruthenium (II) & (III) Schiff base and macrocyclic Schiff base complexes have been extensively studied in last few years due to their importance as biochemical and analytical reagents<sup>40</sup>. But ruthenium (II) macrocyclic Schiff base complexes are less known e.g. Spectroscopic data studies and structures of trans-Ru(II) and Ru(III) bis (cyanide) complexes sustained by tetradentate macrocyclic tertiary amine ligand<sup>41</sup>; N-macrocyclic complexes of Ru(II) & Ru(III); tetraaza macrocyclic Ru(II) complexes: synthesis, spectral and catalytic studies<sup>42</sup>; the versatile Ru II/Ru III tetraaza macrocyclic complexes and their nitrosyl derivative<sup>43</sup>; Ru(II) & (III) complexes with cyclam and related species<sup>44</sup>; Ru(II)/(III) and oxovanadium (IV) complexes with macrocyclic schiff base complexes; Ru(II) complexes of a new tetrapyrazolic macrocyclic; some new polynucleating ligands containing Ru(II) complexes incorporating terpyridyl and macrocyclic aza-crown binding sites. Recently some reviews on macrocyclic ligands have been also published<sup>45</sup>.

Shankar *et al.*,<sup>46</sup> have been synthesised various ruthenium (II) complexes with macrocyclic Schiff base ligands derived from orthophthaldehyde and different diamines. Characterised and used as catalysts for the reduction of pralidoxime to its amino derivatives.

In this present communication, fifteen macrocyclic schiff base ligands will be synthesised by condensation reaction of 2,5-diformyl furan or furil or phenanthrene 9,10-dione with different aliphatic diamines  $\text{NH}_2(\text{CH}_2)_n\text{NH}_2$  i.e.  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  or  $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  or  $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  or  $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  or  $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  and their ruthenium(II) metal

complex through template synthesis in 2:2:1 molar ratio respectively.

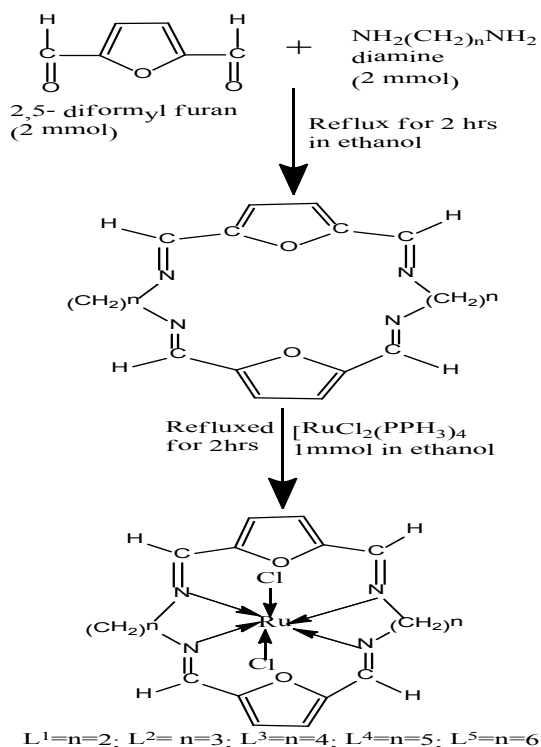
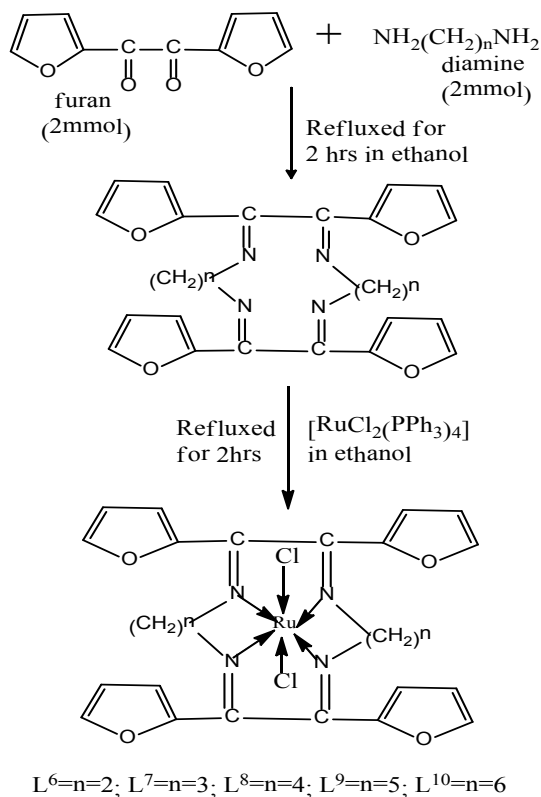
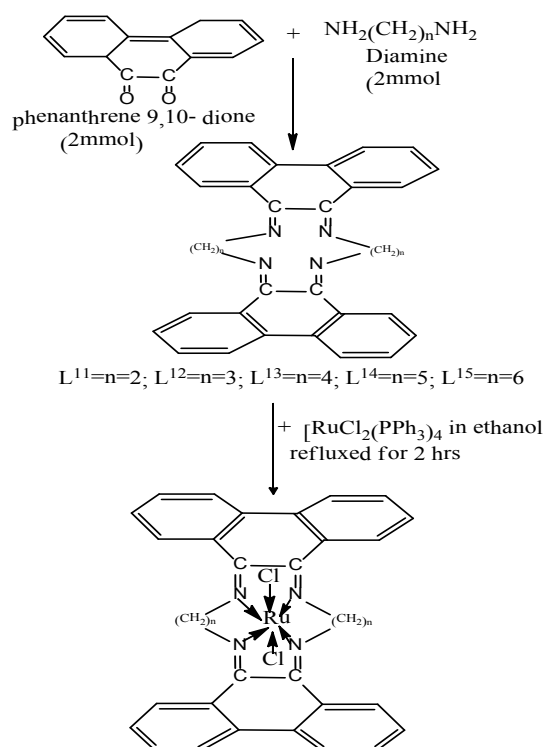
## EXPERIMENTAL

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (Johnson Matthey & Co, Ltd; triphenylphosphine Merck, Mumbai); ethanol (Merck, Mumbai); dichloromethane (Aldrich) and acetone (Aldrich) were AR Grade and used after purification and dried. Solvents were distilled from relevant drying agents immediately in advance of use.  $[\text{RuCl}_2(\text{PPh}_3)_4]$  was prepared by published method.

Melting points were determined by using in sealed capillary tube on Melting point apparatus. The C and H were determined by CDRI, LUCKNOW, INDIA. Nitrogen and chlorine were determined by Kjeldahl's and Volhard's methods respectively. Molar conductivity was measured on Elico-CM 82 conductivity bridge in acetone at room temperature. IR spectra were recorded on Perkin-Elmer 1000 IR spectrometer using KBr/CsI pellets. Electronic spectral measurements were recorded on Elico SL159 spectrophotometer in the range 300-1000 nm. Magnetic measurements were carried out on a Cahn 2000 electro balance by Faraday Method using  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as calibrant. Pascal constants were used for diamagnetic corrections. Kratos analytical Axis Supra ESCA i.e. X-ray photoelectron spectroscopy i.e. XPS instrument equipped with monochromatised Alka (1486.6 eV) source is used. All the peaks were rectified for charging with reference to C1S peak 284.8 eV and counterd with Shirley background and a union of Gaussian and Lorentzian line-shapes, using ESCAPE software.

### Preparation of $[\text{RuCl}_2 \cdot \text{L}^{1-15}]$ complexes

2,5-diformylfuran or furil or phenanthrene 9,10-dione was mixed in dry ethanolic solution of  $\text{NH}_2(\text{CH}_2)_n\text{NH}_2$  (2 mmol) (where (2 mmol)  $n=2$  or 3 or 4 or 5 or 6) and refluxed for 2 h for preparation of ligands  $\text{L}_1$  to  $\text{L}_{15}$ . In this resulting each solution poured  $[\text{RuCl}_2(\text{PPh}_3)_4]$  (1 mmol) i.e. 1:1 molar ratio and again refluxed for about 2 hours. The resulting precipitate was filtered and recrystallised by benzene: pet-ether (9:1) ratio (Figures 1-3).

Fig. 1. Preparation of  $[\text{RuCl}_2\text{L}^{1-5}]$  complexesFig. 2. preparation of  $[\text{RuCl}_2\text{L}^{6-10}]$  complexesFig. 3. Preparation of  $[\text{RuCl}_2\text{L}^{1-15}]$  complexes

## RESULTS AND DISCUSSION

Fifteen tetraaza macrocyclic complexes containing Ru(II) were synthesised by interaction of  $[\text{RuCl}_2(\text{PPh}_3)_4]$  with fifteen macrocyclic Schiff base ligands ( $\text{L}_1$  to  $\text{L}_{15}$ ). The complexes were soluble in DMF, DMSO and chloroform. The elemental analysis (C, H, N and Cl) were consistent within  $\pm 0.5\%$  with the suggested structure of the complexes. The molar conductance values were found to be below ( $12.0\text{--}20.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) recommending the non electrolytic nature of the complexes<sup>47</sup>.

In these entire  $[\text{RuCl}_2\text{L}^{1-15}]$  complexes IR band due to  $\nu_{\text{C}=\text{N}}$  was shifted towards lower side about  $20\text{--}40 \text{ cm}^{-1}$  with respect to the ligand spectra and was obtained in the range of  $1600\text{--}1580 \text{ cm}^{-1}$ . A low intensity band in the region of  $520\text{--}500 \text{ cm}^{-1}$  was observed due to  $\nu_{\text{Ru-N}}$  vibration confirm that ligands coordinate to Ru metal ion through nitrogen of C=N group in all these complexes<sup>48</sup>. Only one band was observed in the range of  $320\text{--}300 \text{ cm}^{-1}$  in IR spectra of all these complexes indicating the presence of two chloride ions in trans position around ruthenium ion<sup>49</sup>. All the Characteristic IR bands were also observed due to aromatic rings in the expected region in all these  $[\text{RuCl}_2\text{L}^{1-15}]$  complexes<sup>49</sup>.

The ground state of Ru(II)  $t_{2g}^6$  electronic configuration is  $^1A_{1g}$ . For octahedral Ru(II) complexes four electronic transition are possible i.e.  $^1A_{1g} \rightarrow ^3T_{1g}$ ;  $^1A_{1g} \rightarrow ^3T_{2g}$ ;  $^1A_{1g} \rightarrow ^1T_{1g}$  and  $^1A_{1g} \rightarrow ^1T_{2g}$ . In each complexes of  $[RuCl_2(L^{1-15})]$  two electronic bands were observed in the region 200-530 nm. These electronic bands have been assigned to the spin allowed  $^1A_{1g} \rightarrow ^1T_{1g}$  transition at lower wavelength (460-520 nm) based on molar extinction coefficient.

The another high intensity band at 280-290 nm region has been assigned due to charge transfer transition originated from the excitation of an electron from the metal  $t_{2g}$  level to the unfilled molecular orbital derived from the  $\pi^*$  level of the ligands. All these  $[RuCl_2(L^{1-15})]$  complexes have shown negative magnetic susceptibility and magnetic moment values below then 1.0 BM at room temperature corresponding to diamagnetic nature.

**Table 1: Physical and Analytical data of  $[RuCl_2(L^{1-15})]$  Complexes**

Sr. No	Complexes	% found (Calculated)				$\Delta M$ Ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>
		C	H	N	Cl	
1	$[RuCl_2(L^1)]$	41.4	3.2	11.6	15	10
		-41.5	-3.3	-11.8	-15	
2	$[RuCl_2(L^2)]$	43.4	4	11	14.2	12
		-43.5	-4	-11.2	-14.3	
3	$[RuCl_2(L^3)]$	42.6	4.4	10.6	13.4	18
		-42.7	-4.5	-10.6	-13.5	
4	$[RuCl_2(L^4)]$	47.6	5	10	12.6	16
		-47.8	-5	-10.1	-12.8	
5	$[RuCl_2(L^5)]$	50.4	5.4	9.4	12	10
		-50.5	-5.4	-9.4	-12	
6	$[RuCl_2(L^6)]$	54.2	3.6	10.5	13.4	12
		-54.4	-3.7	-10.5	-13.4	
7	$[RuCl_2(L^7)]$	56	4.2	10	12.6	14
		-56	-4.3	-10	-12.7	
8	$[RuCl_2(L^8)]$	69	5.6	11.4	14.6	16
		-69.2	-5.7	-11.5	-14.6	
9	$[RuCl_2(L^9)]$	30.6	4	7	9	12
		-30.7	-4.4	-7.1	-9	
10	$[RuCl_2(L^{10})]$	59.8	3.2	11.6	15	18
		-59.9	-3.3	-11.8	-15	
11	$[RuCl_2(L^{11})]$	68	4.8	7	9	20
		-68	-4.9	-7.1	-9	
12	$[RuCl_2(L^{12})]$	68.6	4.6	9.2	11.8	18
		-68.8	-4.7	-9.4	-11.9	
13	$[RuCl_2(L^{13})]$	69.4	5	9	11.2	16
		-69.5	-5.1	-9	-11.4	
14	$[RuCl_2(L^{14})]$	71.2	4	8.6	11	14
		-71.3	-4.4	-8.7	-11.1	
15	$[RuCl_2(L^{15})]$	75	4.2	8.6	11	12
		-75.1	-4.3	-8.7	-11.1	

**Table 2: Infrared Spectral data of  $[RuCl_2(L^{1-15})]$  Complexes**

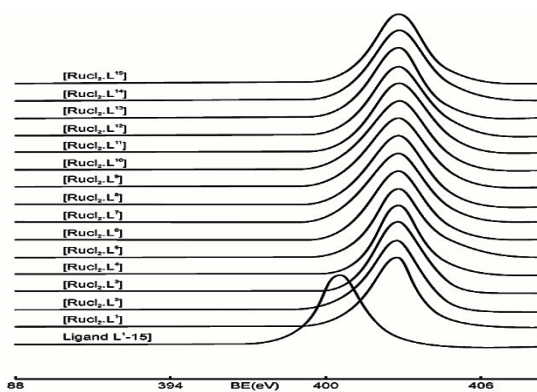
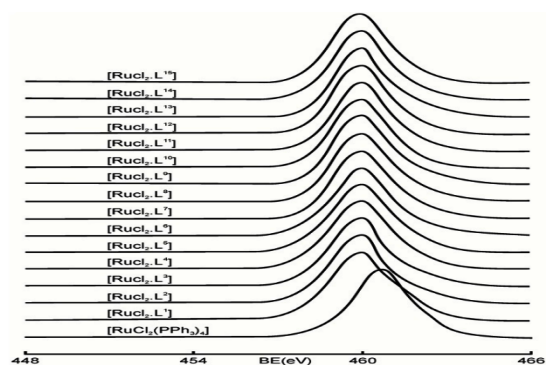
Sr. No	Complex	Selected IR bands (cm <sup>-1</sup> )		
		$V_{C=N}$	$V_{Ru-N}$	$V_{Ru-Cl}$
1	$[RuCl_2(L^1)]$	1580	520	320
2	$[RuCl_2(L^2)]$	1570	515	310
3	$[RuCl_2(L^3)]$	1575	518	305
4	$[RuCl_2(L^4)]$	1580	515	316
5	$[RuCl_2(L^5)]$	1570	500	300
6	$[RuCl_2(L^6)]$	1580	510	315
7	$[RuCl_2(L^7)]$	1580	505	305
8	$[RuCl_2(L^8)]$	1580	500	320
9	$[RuCl_2(L^9)]$	1600	515	315
10	$[RuCl_2(L^{10})]$	1600	518	320
11	$[RuCl_2(L^{11})]$	1590	510	320
12	$[RuCl_2(L^{12})]$	1580	508	315
13	$[RuCl_2(L^{13})]$	1600	515	310
14	$[RuCl_2(L^{14})]$	1580	520	305
15	$[RuCl_2(L^{15})]$	1580	515	320

**Table 3: Ru3p<sub>1/2,3/2</sub>; N<sub>1s</sub> and Cl<sub>2p</sub> binding energies (eV) in ligand; [RuCl<sub>2</sub>(L<sup>1-15</sup>)] complexes**

Sr. No	Ligand & Complexes	Ru3P <sub>1/2,3/2</sub>		N <sub>1s</sub>	Cl <sub>2p</sub>
		Ru3P <sub>1/2</sub>	Ru3P <sub>3/2</sub>		
1	L <sub>1</sub>	---	---	400.6	---
2	L <sub>2</sub>	---	---	400.6	---
3	L <sub>3</sub>	---	---	400.6	---
4	L <sub>4</sub>	---	---	400.6	---
5	L <sub>5</sub>	---	---	400.6	---
6	L <sub>6</sub>	---	---	400.6	---
7	L <sub>7</sub>	---	---	400.6	---
8	L <sub>8</sub>	---	---	400.6	---
9	L <sub>9</sub>	---	---	400.6	---
10	L <sub>11</sub>	---	---	400.6	---
11	L <sub>11</sub>	---	---	400.6	---
12	L <sub>12</sub>	---	---	400.6	---
13	L <sub>13</sub>	---	---	400.6	---
14	L <sub>14</sub>	---	---	400.6	---
15	L <sub>15</sub>	---	---	400.6	---
16	[RuCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>4</sub> ]	482.8	460.8	---	201.6
17	[RuCl <sub>2</sub> L <sup>1</sup> ]	482	460	402.8	202.8
18	[RuCl <sub>2</sub> L <sup>2</sup> ]	482	460	402.8	202.8
19	[RuCl <sub>2</sub> L <sup>3</sup> ]	482	460	402.8	202.8
20	[RuCl <sub>2</sub> L <sup>4</sup> ]	482	460	402.8	202.8
21	[RuCl <sub>2</sub> L <sup>5</sup> ]	482	460	402.8	202.8
22	[RuCl <sub>2</sub> L <sup>6</sup> ]	482	460	402.8	202.8
23	[RuCl <sub>2</sub> L <sup>7</sup> ]	482	460	402.8	202.8
24	[RuCl <sub>2</sub> L <sup>8</sup> ]	482	460	402.8	202.8
25	[RuCl <sub>2</sub> L <sup>9</sup> ]	482	460	402.8	202.8
26	[RuCl <sub>2</sub> L <sup>10</sup> ]	482	460	402.8	202.8
27	[RuCl <sub>2</sub> L <sup>11</sup> ]	482	460	402.8	202.8
28	[RuCl <sub>2</sub> L <sup>12</sup> ]	482	460	402.8	202.8
29	[RuCl <sub>2</sub> L <sup>13</sup> ]	482	460	402.8	202.8
30	[RuCl <sub>2</sub> L <sup>14</sup> ]	482	460	402.8	202.8
31	[RuCl <sub>2</sub> L <sup>15</sup> ]	482	460	402.8	202.8

The binding energies (eV) of prepared ligands i.e. L<sup>1-15</sup>; [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] and [RuCl<sub>2</sub>(L<sup>1-15</sup>)] in Table 1 (Figs. 4-6) for Ru3p<sub>1/2,3/2</sub>, N<sub>1s</sub> and Cl2p photoelectron peaks. It was observed that Ru3p<sub>1/2,3/2</sub> binding energies in starting material [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] were higher (BE = ~ 482.8 eV and

460.8 eV for Ru3p<sub>1/2</sub> and Ru3p<sub>3/2</sub>) than in prepared [RuCl<sub>2</sub>L<sup>1-15</sup>] complexes (Ru3p<sub>1/2</sub> BE = 482.0 eV and Ru3p<sub>3/2</sub> BE 460.0 eV); suggesting that electron density in ruthenium metal ion is more in prepared [RuCl<sub>2</sub>L<sup>1-15</sup>] complexes than in [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] due to coordination<sup>50</sup> (Figures 4-6).

Fig. 4. Ru3p<sub>1/2</sub> binding energies (eV) in [RuCl<sub>2</sub>(L<sup>1-15</sup>)] complexesFig. 5. Ru<sub>3p</sub><sup>3/2</sup> binding energies (eV) in [RuCl<sub>2</sub>(L<sup>1-15</sup>)] complexes prepared [RuCl<sub>2</sub>(L<sup>1-15</sup>)] metal complexes

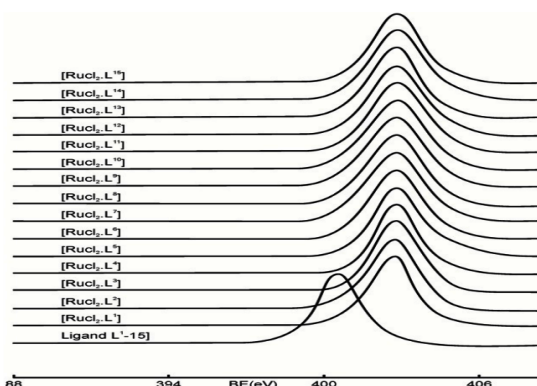


Fig. 6.  $N_{1s}$  binding energies (eV) in Ligands and  $[RuCl_2(L^{1-15})]$  complexes prepared

The  $N_{1s}$  photoelectron spectra of all these  $[RuCl_2(L^{1-15})]$  complexes have shown only one signal symmetrical photoelectron peak towards higher binding energies side (  $BE = \sim 402.8$  eV) than  $N_{1s}$  photoelectron peak of each ligand ( $\sim BE = 400.6$  eV) suggesting all four nitrogen atoms of each ligand is coordinated with ruthenium (II) metal ion.<sup>50</sup> (Fig. 6) & Table 1) The  $Ru_{3s}$  photoelectron peak in all these prepared  $[RuCl_2(L^{1-15})]$  metal complexes. have shown symmetrical peak at 584.6 i.e. have not shown multiple splitting diamagnetic nature<sup>50</sup>. The  $Cl_{2p}$  photoelectron spectra of all these  $[RuL_2(L^{1-15})]$  complexes have shown one sharp peak at  $BE \sim$

202.4-202.0 eV; suggesting inner sphere chlorine atom in trans position<sup>50</sup>.

## CONCLUSION

In the present paper, fifteen Ru(II) complexes of the type  $[RuCl_2L^{1-15}]$  have been synthesized and characterized with fifteen tetraaza macrocyclic ligands. On account of analytical and spectral statistics octahedral geometry were provisionally proposed for all of these complexes.

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## Conflicts of interest

The authors declare no conflict of interest in the present research work.

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