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Tetraaza Macrocyclic Ruthenium (II) Complexes: Synthesis, Spectral and Catalytic Studies

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Abstract : A new family of Tetraazamacrocyclic Ru(II) complexes $[RuCl_2(L)]$ (where L = N_4 donor macrocyclic ligands) have been synthesized by the reactions of $[RuCl_2(DMSO)_4]$ with some of macrocyclic Schiff base ligands containing N_4 donor groups. The complexes were characterized by elemental analysis, IR, ^1H, ^{13}C NMR, mass, electronic, molar conductance and magnetic susceptibility measurements. An octahedral geometry has been proposed for all complexes. These compounds were used as catalysts for the reduction of pralidoxime to its amino derivative. The reduced pralidoxime was also characterized by spectral analysis and it was determined spectrophotometrically by treating with ninhydrin reagent and the percent yields were found to be in the range of 79.12- 86.58

Keywords: Ru(II) complexes; N_4 macrocyclic Schiff bases; pralidoxime; catalyic studies

1. Introduction

Macrocycles and macrocyclic metal compounds design and synthesis is one of the fascinating areas of current research to the inorganic chemists all over the world because of their biological, analytical and catalytical applications[1-7] . The research field dealing with transition metal complexes with macrocyclic Schiff base has expanded enormously and embraced wide and diversified subjects comprising vast areas of organometallic compounds[8] and various aspects of biocoordination chemistry[9] .Ruthenium Schiff base complexes have been amongst the most widely studied organometallics in the past few years, since they are important as biochemical and analytical reagents[10,11] .Macrocyclic Schiff base compounds can be synthesized from orthophthalaldehyde (OPA) due to the presence of two aldehyde groups in it. These compounds are then treated with metal salt to get macrocyclic metal compounds. The existing OPA based macrocyclic metal compounds were synthesized by the direct treatment of OPA, diamine and metal salts[12-15]. Since, the authors group synthesized the macrocyclic metal compounds from OPA by the initial preparation of macrocycle followed by its treatment with metal salts[1-5].

Pralidoxime belongs to a family of compounds called oximes that bind to organophosphate-inactivated acetylcholinesterase. It is used to combat poisoning by organophosphates or acetylcholinesterase inhibitors (nerve agents), in conjunction with atropine. Our continuous efforts in developing new catalytic methods[16-18] lead to the development of rapid and selective method for the reduction of oxime containing drug viz. pralidoxime iodide (PI) to its amine derivative viz. 2-aminomethyl-1-methyl-pyridinium iodide by using macrocyclic Ru(II) complexes in the presence of ammonium formate at room temperature in the present investigations. The reduced pralidoxime iodide (RPI) was treated with ninhydrin (NH) [19] to get blue colored product which was exploited for the spectrophotometric determination of the percent yields of RPI formed during reduction process. This method was successfully applied for the reduction of pralidoxime iodide in pharmaceuticals. In connection with previous investigations[2-5,20], on the coordinating properties of tetraaza macrocycles, and in order to isolate new transition metal complexes with catalytic activities, we have studied the synthesis, spectroscopic and catalytic aspects of tetraaza macrocyclic complexes of Ru(II) derived from orthophthalaldehyde with various diamines.

2. Experimental

2.1. Materials and Methods

$RuCl_3.3H_2O$ (Johnson Matthey & Co. Ltd), Dimethyl sulphoxide (DMSO) (Merck, Mumbai), methanol (Merck, Mumbai), and dichloromethane (Qualigens) were used as such. All solvents used were of AR grade. An analytically pure sample of cis-$[RuCl_2(DMSO)_4]$ was prepared by published method[21] .Six macrocyclic ligands viz. 7,8,9,18,19,20-

hexahydrodibenzo[*g*,*p*][1,2,4,5,10,11,13,14]-octaazacyclooctadecine-8,19-dione[HBOADO],7,8,17,18-tetrahydrodibenzo[*f*,*n*][1,2,4,9,11,12]-hexaazacyclohexadecine-8,17-dione[TBACD],3,4,5,6,7,8,9,10-octahydro-2,5,8,11-benzotetra azacyclotetradecine[OBACD],7,8,9,18,19,20-hexahydrodibenzo[*g*,*p*][1,2,4,5,10,11,13,14]-octa azacyclooctadecine-8,19-dithione[HBOADT],7,16-dihydrodibenzo[*e*,*l*][1,3,8,10]tetraazacyclo tetradecine-7,16-dithione[DBACDT] and 7,8,17,18-tetrahydrodibenzo[*f*,*n*][1,2,4,9,11,12]hexa azacyclohexadecine-8,17-dithione[TBAHD] were newly prepared and characterized. Ammonium formate solution (Merck, 0.1 M) was prepared by dissolving 0.63 g in 100 ml of double distilled water. Ninhydrin solution (Merck, 0.1 M) was prepared by dissolving 1.78 g in 100 ml of double distilled water. Standard stock solution of pralidoxime iodide (1 mg/ml) was prepared by dissolving 100 mg of pure pralidoxime iodide in 100 ml of double distilled water. This solution was diluted with the same solvent to get the working pure drug solution of 100 µg/ml. Standard pharmaceutical solution of pralidoxime iodide (1 mg/ml) was prepared by diluting 4 ml of injection solution (equivalent to 100 mg) to 100 ml with double distilled water. This solution was diluted with the same solvent to get the working pharmaceutical solutions of 100 µg/ml.

2.2. Measurements

The melting points of all the macrocyclic ligands and macrocyclic metal compounds were obtained on a Buchi- 510 melting point apparatus. The percentages of carbon, hydrogen, nitrogen in macrocyclic metal compounds were determined using a Perkin Elmer 2400 elemental analyzer. The IR spectra were recorded using KBr/CsBr pellet technique in a Perkin-Elmer 283 IR spectrophotometer. Brucker WH 300 (200 MHz) and Brucker WH 270 (67.93 MHz) spectrometers were used for ^{1}H NMR and ^{13}C NMR measurements. The NMR spectra were recorded using $CDCl_3$/DMSO-d_6 solvents (different ratios of these solvents) operating at 298 ^{0}K. MICROMASS-7070 spectrometer was used to obtain mass spectra. UV-Visible spectra were recorded with a Shimadzu UV-160A, a UV-Visible double beam spectrophotometer equipped with matched quartz cells of path length 1 cm. Conductance measurements were done on 10^{-3} M solution of compounds in dichloromethane at room temperature using Digisun Digital conductivity meter model DL-909. Gouy balance calibrated with $Hg[Co(NCS)_4]$ was used for the determination of magnetic susceptibilities of complexes in solid state at room temperature.

2.3. Synthesis of macrocyclic Ru(II) compounds

A solution (25 ml) of $[RuCl_2(DMSO)_4]$ (0.001 mol., 0.480g in toluene) and 25 ml of the respective ligand solution (0.001 mol., viz. in methanol) were mixed and stirred magnetically at $60^{o}C$. The suspension was refluxed for one hour, when the whole suspension dissolved giving a homogeneous solution. The resulting solution was evaporated a small volume under vacuum and the products precipitated with diethyl ether. The resulting precipitate was separated by suction filtration, washed with diethylether; vacuum dried to get a crystalline compound and was recrystallized using methanol and diethylether solvent mixture.

2.4. Catalytic reduction method

In a 100 ml round bottom flask, 5 ml of pralidoxime iodide, 5 ml of ammonium formate and $[RuCl_2(L)]$ (0.01 mmol) were taken. The contents of the flask were stirred for 15 min. at room temperature. The contents of the flask were cooled and transferred separately into 20 ml calibrated tubes. Now the reduced drug is speared from the catalyst using a column. The reduced drug is dissolved in 10 ml of methanol and transferred separately into 20 ml calibrated tubes. Then, 1 ml of ninhydrin solution was added and heated for 5 min at 70 ^{0}C. The tubes were cooled and the total volumes were made up to 20 ml with double distilled water and kept aside for 5 min. The absorbance of the colored solution was measured at 600 nm against the reagent blank. The amount of RPI formed during the reduction process was estimated from the calibrated curve. The procedure was repeated by changing macrocyclic Ru(II) compounds one by one. This procedure was also applied for pharmaceutical solutions. The separated catalyst is dissolved in 20 ml of methanol, then KI (0.01 mmol) and 5 ml of hydrochloric acid (0.1 N) were added and heated for 30 min. to get the original catalyst. This is recrystallized using dichloromethane.

3. Results and Discussion

A series of six tetraaza macrocyclic Ru(II) complexes were synthesized by treating $[RuCl_2(DMSO)_4]$ with the six macrocyclic Schiff base ligands. All the complexes are stable to the atmosphere. The complexes are soluble in chloroform, DMSO, DMF and aqueous methonal. The elemental analyses (Table 1) are consistent with the proposed structure of the complexes. All the complexes were found to have diamagnetic character assigning +2 oxidation state to ruthenium. The molar conductance values for the Ru(II) complexes (10^{-3} M) are determined in dichloromethane[2] . These values are found to be low (12.0-18.5 $ohm^{-1}cm^{2}mol^{-2}$) indicating non-electrolytic nature of the complexes (Table 1).

3.1. Infrared spectral data

The main bands and their assignments are listed in Table 2. In the IR spectra of macrocyclic Ru(II) complexes a medium intensity band due to $\upsilon_{(C=N)}$ was shifted towards lower side about 20-35 cm^{-1} compared to the ligand spectra and was appeared in the

range of 1590-1570 cm^{-1} [22]. The appearance of a lower intensity band in the region of 520-502 cm^{-1} corresponds to the $\upsilon_{(M-N)}$ vibration supports the fact that the ligands coordinate to the metal ions through the nitrogen of C=N group in all the complexes[12]. However, in the complex **3** $\upsilon_{(N-H)}$ band was observed at 3320 cm^{-1}. This band was shifted towards lower side about 25 cm^{-1} compared to the ligand spectra indicates the coordination of the metal through nitrogen of NH group[23,24]. A band present in the range of 320-300 cm^{-1} in the spectra all complexes indicating the presence of two chlorides in trans position around ruthenium center[3]. The characteristic bands due to the $\upsilon_{C=O}/\upsilon_{C=S}$ in the spectra of respective macrocyclic Ru(II) compounds were remain almost unshifted[3] . All the characteristic bands due to the aromatic rings were also present in the expected regions[3] in all the macrocyclic Ru(II) compounds.

3.2. NMR spectral analysis

In the ^1H NMR spectra of the macrocyclic Ru(II) compounds the integral intensities of each signal were found to agree with the number of different types of protons present. In all the ligands signals were appeared in the range of 8.10-8.43 δ due to CH=N protons. However, in the spectra of macrocyclic Ru(II) compounds, these signals were observed in the up field regions of 8.20-8.65 δ confirming the coordination of nitrogen atom of this group to Ru(II) ion[23]. In the spectrum of the complex-**3** a broad signal was observed at 5.93 δ due to NH proton, which was shifted from 5.60 δ of ligand indicating the coordination of NH group[25]. There is no appreciable change in the peak positions corresponding to aromatic protons[14] .

^{13}C NMR signals for the macrocyclic Ru(II) compounds are assigned by the comparison with the spectra of corresponding macrocyclic ligands and the chemical shifts in ^{13}C NMR spectra revealed a consistent pattern. In the spectra of Ru(II) complexes, a down field shift of CH=N group was observed in the range of 145.8-163.5 δ, indicate that all the ligands coordinate through the nitrogen atoms [26]. Appreciable changes in peak positions were not observed with respect to aryl carbons and carbons adjacent to oxygen/sulphur atom[14]. The ^1H and ^{13}C NMR data of macrocyclic Ru(II) complexes is given in Table 3.

3.3. Mass spectral analysis

In the mass spectra of respective macrocyclic Ru(II) compounds, molecular ion peaks, were observed at different m/z (M^+) values. This data is in good agreement with the respective molecular formulae. The isotope pattern calculations that represent in web-based and windows-based application to view the mass spectrum. The existing systems face a number of problems, such as slow performance of viewing the output, incomplete graph interface which not user friendly and low capability in output the values of large molecules such as inorganic complexes. Thus, to overcome this problem isotope pattern calculations are developed. This helps to calculate the exact molecular formula and molecular weights of the complexes. The isotope patterns of all the macrocyclic Ru(II) complexes are given Table 4.

3.4. Electronic spectral analysis

The macrocyclic Ru(II) complexes are diamagnetic, indicating the presence of the ruthenium +2 oxidation state. The ground state of Ru(II) (t_{2g}^6 configuration) is $^1A_{1g}$. For a hexacoordinated Ru(II) complex, four transitions corresponding to $^1A_{1g} \rightarrow {}^3T_{1g}$; $^1A_{1g} \rightarrow {}^3T_{2g}$; $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ are possible. In the electronic spectra of all the complexes, two bands are observed in the 200-520 nm regions. These bands at the longer wavelength (465-520 nm) have been assigned to the spin allowed $^1A_{1g} \rightarrow {}^1T_{1g}$ transition based on molar extinction coefficients[27]. The other high intensity band, at 260-290 nm region has been assigned to the charge-transfer transition arising from the excitation of an electron from the metal t_{2g} level to the unfilled molecular orbital derived from the π* level of the ligands, in accordance with the assignments made for other similar octahedral ruthenium (II) complexes [27-28].

On the basis of analytical and spectral data, octahedral structures (Scheme 1) have been tentatively proposed for all of these complexes.

3.5. Catalytic reduction

3.5.1. Optimum conditions

The experimental parameters were optimized to obtain maximum yields and absorbance in the reduction and spectrophotometric procedures. In the preliminary investigations, reducing agents such as Zn/ammonium formate and Mg/ammonium formate were used along with present catalysts $[RuCl_2(L)]$ to reduce the oxime group of pralidoxime iodide to amino group. The percent yields of amino derivative of the drug was found to be high when $[RuCl_2(L)]$ is used as catalyst (8-12 min, 79.12-86.58 %,), Zn/ammonium formate - 20 min, 71.22 %, Mg/ ammonium formate - 20 min, 70.12 %). 0.01 mmol of catalyst is found to be sufficient for the reaction. The use of ammonium chloride for the reduction of nitro compounds to amines provoked to investigate the reduction by replacing ammonium chloride by ammonium formate, which performs the conversion of oximes to amines at a faster rate. The complete conversion requires at least 2-3 hours at reflux temperature if ammonium chloride is used. This may be due to the fact that the solubility of ammonium chloride is very poor compared to ammonium formate and also in the case of ammonium formate, formate ion also provides hydride ion for the reduction. Studies were also carried out to determine the optimum conditions for reduction. An excess of 4-6 ml of ammonium formate was found to be ideal. The

rate of transfer hydrogenation decreased substantially when only one ml of hydrogen donor was used. On the

other hand, a large excess of ammonium formate produced only a marginal increase in the rate of reaction compared to that observed when 4-6 ml were used. Optimal ratio of catalyst to substrate was found to be 1:1. A control experiment was carried out using oximes with ammonium formate or ammonium chloride, but without macrocyclic Ru(II) compound and the pralidoxime iodide was recovered in almost quantitatively. This clearly indicates that ruthenium catalyses the reaction. In addition, the formed amino derivative of pralidoxime iodide was determined by treating it with ninhydrin[29] along with other color reagents viz. 1-chloro-2,4-dinitrobenzene[30], l-fluoro-2,4dinitrobenzene[31] and m-dinitrobenzene[32]. Since, ninhydrin produces high λmax and molar absorptivity values (600 nm, $3.21x10^3$ l mol^{-1} cm^{-1}) over 1-chloro-2,4-dinitro benzene (420 nm, 1.58 $x10^3$ l mol^{-1} cm^{-1}), l-fluoro-2,4dinitrobenzene (400 nm, 1.18 $x10^3$ l mol^{-1} cm^{-1}) and m-dinitrobenzene (460 nm, 1.01 $x10^3$ l mol^{-1} cm^{-1}), it was preferred for the color development. The effect of ninhydrin concentration on the color development was investigated. For this purpose, 1-3 ml of ninhydrin was added. It was observed that the highest and most stable absorbance was obtained with 1 ml, beyond which the absorbance became constant. Therefore, 1 ml of the reagent was used as an optimum value for color development. λmax of the color product was found to be 600 nm. Maximum color was formed within 10 min and color product was stable up to one hour.

3.5.2. Interference studies

The extents of interferences by additives were determined by measuring the absorbance of a solution containing 5 ml of pralidoxime iodide and various amounts of additives which often accompany the pharmaceuticals. Majority of them do not interfere in the reduction as well as determination. An error of 2% in the absorbance readings were considered as tolerable limits.

3.5.3. Product analysis

The infrared spectra of pralidoxime iodide show a broad peak around 3460 cm^{-1} due to the stretching of OH group. It does not show any sharp signals around 3290 cm^{-1} indicating the absence of aliphatic primary amino group. PI contain a peak at 1620 cm^{-1} due to the stretching of C=N bond. The disappearance of this peak and appearance of a new peak at 1480 cm^{-1} indicates the absence of C=N and the presence of C-N bond. Similarly, the absence of a band at 3460 cm^{-1} in RPI due to the presence of N-O bond indicates absence of oxygen atom in RPI. The appearance of strong absorption band around 3300 cm^{-1} in RPI indicates the N-H stretching of aliphatic primary amino group.

The ^1H NMR spectra of PI show peaks at 8.80 δ and 8.59 δ corresponding to CH=N and N-O-H protons. But, in the ^1H NMR spectra of RPI, these peaks were not appeared indicating the absence of these protons. However, two new peaks were appeared at 3.35 and 5.21 δ indicating the presence of $–CH_2$- and -NH_2 protons, respectively confirming the presence of aliphatic primary amino group in RPI. Reduction of aldoxime group to aliphatic primary amino group is further confirmed by ^{13}C NMR spectral analysis. The spectra of PI show a peak at 157.8 δ corresponding to the carbon belonging to CH=N group. But, in the spectra of RPI, this peak was not appeared. Instead of this, a new peak was appeared at 43.6 δ indicating conversion of CH=N-OH group to CH_2-NH_2 group.

3.5.4. Chemistry

A plausible mechanism has been proposed for Ru(II) catalyzed reduction of pralidoxime iodide to its reduced product in the presence of ammonium formate is given in Scheme 2. Ninhydrin reagent is used to detect ammonia, primary and secondary amines. It gives a blue colored product (Ruhemenn's purple) with primary amines[29] and yellow orange colored product with secondary amines. Tertiary and quarternary amines cannot be detected by this reagent. Reduced pralidoxime iodide contains a primary aliphatic amino group that reacts with ninhydrin in methanol medium via oxidation-deamination of the primary amino group followed by condensation of the reduced ninhydrin to form the blue colored reaction product (Scheme 2).

The percent yields of RPI with all the macrocyclic Ru(II) compounds were determined spectrophotometrically and results are given in Table 5.

4. Conclusions

In the present communication, we have synthesized and characterized six ruthenium (II) complexes containing tetraaza macrocyclic ligands. Octahedral structures were assigned to these complexes based on analytical and spectral data. These compounds were found to be efficient in the reduction of pralidoxime to its primary amino derivative. This catalytic reduction method was proved to be efficient for reduction of drugs over traditional hydrogenation or reduction methods as it involves mild reaction condition, easy work-up and high degree of selectivity.

Table 1 : Physical, analytical and electronic spectral data of macrocyclic Ru(II) complexes.

Comp. No.	Ru(II) compound/ Molecular formula	Λ_M	Analyses (%) Found (Calculated)			
			C	H	N	Ru
1.	[Ru(HBOADO)Cl_2] $C_{18}H_{16}Cl_2N_8O_2Ru$	17.5	39.50 (39.43)	2.90 (2.94)	20.44 (20.43)	18.53 (18.43)
2.	[Ru(TBACD)Cl_2] $C_{18}H_{14}Cl_2N_6O_2Ru$	13.0	41.73 (41.71)	2.75 (2.72)	16.23 (16.21)	19.56 (19.50)
3.	[Ru(OBACD)Cl_2] $C_{14}H_{20}Cl_2N_4Ru$	15.5	40.36 (40.39)	4.80 (4.84)	13.48 (13.46)	24.20 (24.28)
4.	[Ru(HBOADT)Cl_2] $C_{18}H_{16}Cl_2N_8S_2Ru$	12.0	37.22 (37.24)	2.75 (2.78)	19.40 (19.30)	17.50 (17.41)
5.	[Ru(DBACDT)]Cl_2 $C_{18}H_{12}Cl_2N_4S_2Ru$	18.5	41.49 (41.54)	2.38 (2.32)	10.72 (10.77)	19.47 (19.42)
6.	[Ru(TBAHD)Cl_2] $C_{18}H_{14}Cl_2N_6S_2Ru$	16.0	39.22 (39.28)	2.50 (2.56)	15.22 (15.27)	18.34 (18.36)

Table 2 :Infrared spectral data of macrocyclic Ru(II) complexes.

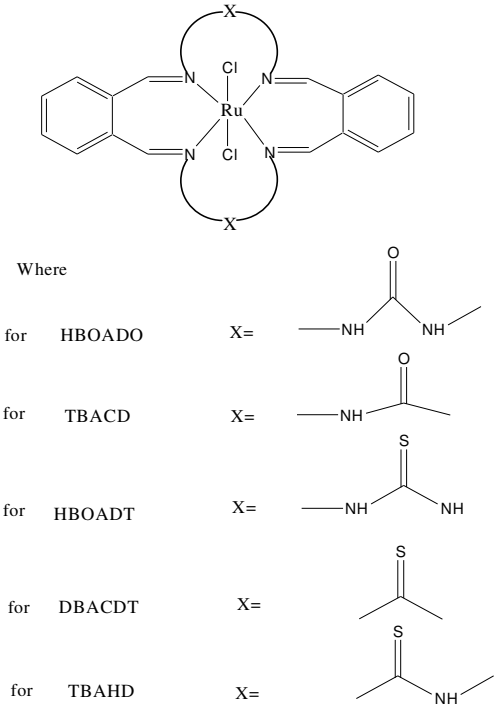
Comp. No.	Ru(II) compound	Selected IR bands (cm^{-1})			
		$\upsilon_{C=N}$	υ_{NH}	υ_{Cu-N}	Anion peaks
1.	[Ru(HBOADO)Cl2]	1588	3320	505	310
2.	[Ru(TBACD)Cl2]	1570	3326	518	300
3.	[Ru(OBACD)Cl2]	1590	3320	520	320
4.	[Ru(HBOADT)Cl2]	1580	3324	514	305
5.	[Ru(DBACDT)Cl2]	1585	-	502	-
6.	[Ru(TBAHD)Cl2]	1575	3383	515	316

Table 3: ^{1}H & ^{13}C NMR spectral data of macrocyclic ruthenium (II) complexes

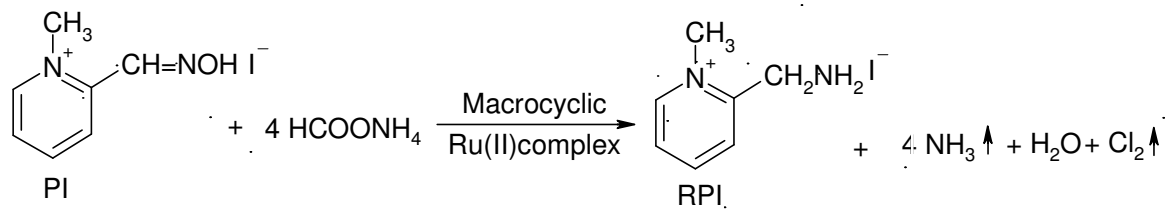
Comp. No.	Ru(II) compound	^{1}H NMR peak position (δ ppm)	^{13}C NMR peak position (δ ppm)
1.	[Ru(HBOADO)Cl2]	5.95 (4H, s, NH), 7.00-8.15 (8H, m, Ar-H), 8.45 (4H, s, CH=N)	130.4, 131.8, 136.5 (12C, Ar-C), 154.6 (4C, CH=N), 175.0 (2C, C=O)
2.	[Ru(TBACD)Cl2]	5.80 (2H, s, NH), 7.10-7.90 (8H, m, Ar-H), 8.65 (4H, s, CH=N)	132.5, 133.8, 134.9, 137.0, (12C, Ar-C), 150.4, 163.5 (4C, CH=N), 156.2 (2C, C=O)
3.	[Ru(OBACD)Cl2]	2.20-2.45 (4H, m, -CH_2), 2.92 (4H, s, -CH_2), 3.40-3.72 (4H, m, -CH_2-), 7.01-7.80 (4H, m, Ar-H), 8.20 (2H, s, CH=N), 5.93 (2H, s, NH)	46.0, 48.0, 61.2 (6C, CH_2), 130.4, 135.6, 136.8 (6C, Ar-C) 156.2 (2C, CH=N)
4.	[Ru(HBOADT)Cl2]	5.88 (4H,s, NH), 7.30-7.82 (8H, m, Ar-H), 8.42 (4H, s, CH=N)	132.2, 134.5, 137.8 (12C, Ar-C), 158.1 (4C, CH=N), 173.7 (2C, C=S)
5.	[Ru(DBACDT)Cl2]	7.10-8.12 (8H, m, Ar-H), 8.55 (4H, s, CH=N)	133.5, 136.8, 137.6, 139.0 (12C, Ar-C), 158.4 (4C, CH=N), 175.2 (2C, C=S)
6.	[Ru(TBAHD)Cl2]	5.80 (2H, s, NH), 7.18-7.99 (8H, m, Ar-H), 8.33 (4H, s, CH=N)	133.6, 134.8, 135.9, 136.7, 137.6, 138.5 (12C, Ar-C), 145.8, 163.2 (4C, CH=N), 176.6 (2C, C=S)

Table 4: Isotope pattern of macrocyclic Ru(II) compounds

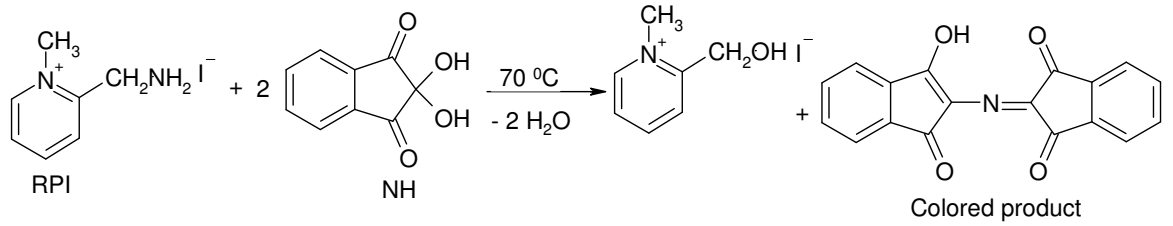
Comp. No.	Molecular formula	Isotope pattern macrocyclic Ru(II) complexes
1.	[Ru(HBOADO)Cl2]	542(12.5%), 544(13.0%), 545(30.5%), 546(38.4%), 547(63.5%), 548(100%,M^+), 549(48.0%), 550(96.0%), 551(25.2%), 552(36.8%)
2.	[Ru(TBACD)Cl2]	512(11.2%), 514(12.5%), 515(31.0%), 516(37.5%), 517(60.2%), 518(100%,M^+), 519(46.5%), 520(95.0%), 521(24.2%), 522(35.3%)
3.	[Ru(OBACD)Cl2]	410(10.5%), 412(11.9%), 413(29.9%), 414(36.8%), 415(61.8%), 417(100%,M^+), 418(97.0%), 419(18.8%), 420(36.3%)
4.	[Ru(HBOADT)Cl2]	574(12.8%), 576(13.8%), 577(28.5%), 578(36.8%), 579(63.5%), 580(99.0%), 581(52.1%), 582(100%,M^+), 583(28.9%), 584(44.0%), 585(11.2%)
5.	[Ru(DBACDT)Cl2]	514(10.8%), 516(13.4%), 517(30.2%), 518(37.5%), 519(63.0%), 520(98.5%), 521(51.2%), 522(100%,M^+), 523(28.5%), 524(43.5%), 585(10.5%)
6.	[Ru(TBAHD)Cl2]	544(12.5%), 546(13.2%), 547(27.5%), 548(36.9%), 549(62.9%), 550(99.2%), 551(50.5%), 552(100%,M^+), 553(28.2%), 554(42.9%), 555(9.5%)



Scheme 1: Representative structures of macrocyclic Ru(II) complexs



Scheme 2: Catalytic reduction of pralidoxime using macrocyclic Ru(II) complex



Scheme 3: Colored product formed between RPI and Ninhydrin.

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