

Synthesis and characterization of some $[\text{RuCl}_3\text{L}^1\text{L}^2]$ complexes with macrocyclic ligands

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Abstract

Ruthenium(III) complex of the type $[\text{RuCl}_3\text{L}^1\text{L}^2]$ (where L^1 =dibenzo 18-crown-6 and L^2 =methionine or leucine or cysteine or serine and isoleucine) was synthesized and characterised by elemental analysis, molar conductivity, IR and XPS i.e. X-ray photoelectron spectroscopy data. A distorted octahedral geometry was also established.

Keywords: Ruthenium, Macrocyclic ligand, X-Ray Photoelectron Spectroscopy.

Introduction

The metals macrocyclic chemistry is increasing more rapidly because of its various applications.¹⁻³ Macrocyclic metals complexes are most important in the coordination chemistry⁴ as well as the bioinorganic chemistry⁵. Several macrocyclic ligands like crown ethers⁶, saturated and unsaturated polyamines and porphyrins⁷⁻⁹ and Robson type tetraaminodiphenol macrocyclic ligands are reported mostly,^{10,11} N4S2 donor macrocyclic ligands^{12,13} and polyazamacrocyclic ligands are reported.^{14,15} The complexes of Schiff base macrocyclic ligands have been studied coordination with different types of metal centres.¹⁶ The condensation reactions are most important in the field of macrocyclic chemistry^{17,40}. Various transition metal ions act as enzyme in different living system and also act as a carrier in macrocyclic ligand environment¹⁸ and various applications in modelling the active sites of metalloenzymes.¹⁹

Macrocyclic metal complexes have lots of beneficial application.^{44,45} Metal ions separation detecting tumor lesions are used as a monoclonal antibodies with a radioactive models,^{21,22} used as a cancer diagnosis,²³⁻²⁵ used as a radiotherapeutic and as a therapeutic,²⁶ used as a catalyst in a reaction²⁷ and used as a pharmacological agents^{28,29}. Macrocyclic metal complexes are used as a contrast enhancing agents in magnetic resonance imaging (MRI),³⁶ used as a agent in NMR,³⁷ used as a agents in relaxation³⁸ as well as used as a RNA cleavage catalyst.³⁹ Discoveries of various types of macrocyclic ligands and their metal complexes have created the supramolecular chemistry.³⁹⁻⁴¹ In the present note, we report the synthesis of ruthenium(III) complexes with some amino acids and the macrocyclic ligands.

Material and Methods

All the chemical reagents were purchased from Sigma Aldrich of high purity and were used with further

purification. Ruthenium trichloride, dibenzo-18-crown-6, methionine, leucine, serine, cysteine and isoleucine were purchased by Sigma Aldrich (AR).

Experimental: The elemental analysis for C,H,N,O, and S was determined on a semimicro scale at CDRI Lucknow, India. Molar conductances of all the complexes were measured at room temperature in acetone by Digisum electronics conductivity bridge. The infrared spectra of the complexes and ligands were recorded in KBr and CSI on Perkin-Elmer 457 spectrometer. The X-ray photoelectron Spectra(XPS) were recorded on a VG scientific ESCA-MK II electron spectrometer.

Synthesis of macrocyclic ligands: A solution of catechol(1mmol) was mixed with hot solution of bischloroethyl ether(1mmol) with constant stirring. The solution was heated at 50°-60° C (pH 8) for 3h. On cooling at 0°C, a solid product was precipitated out. It was filtered and washed several times with cold ethanol. The resultant precipitate was filtered and recrystallized into ether:ethanol(9:1) ratio(Figure I).

Synthesis of metal complexes: Hot methanolic solution of RuCl_3 (1mmol) and L^1 = dibenzo-18 crown-6(1mmole) was refluxed for 3 hrs and L^2 =methionine or cysteine or leucine or isoleucine or serine(1 mmol) was added dropwise to solution and was refluxed for 3 hrs and then clear solution was allowed to cool at 0°C. The solid product precipitated was filtered, washed in methanol, diethyl ether and dried under vacuum (Figure II).

Results and Discussion

The newly synthesized compounds $[\text{RuCl}_3\text{L}^1\text{L}^2]$ (L^1 =dibenzo 18 crown6 and L^2 = methionine or leucine or cysteine or serine or isoleucine) are brownish red colour. They are soluble in common organic solvents and stable towards atmospheric oxygen and moisture. These compounds are stable at room temperature even on long standing. The elemental analysis of C,H,N was obtained within $\pm 0.5\%$ (calculated and found value). Molar conductivity was observed in the range of $30 \text{ ohm}^{-1}\text{cm}^2 \text{ mol}^{-1}$ suggesting non-electrolyte. $\nu_{\text{Ru-Cl}} \sim 330 \text{ cm}^{-1}$, $\nu_{\text{Ru-N}} \sim 440 \text{ cm}^{-1}$, $\nu_{\text{Ru-S}} \sim 540 \text{ cm}^{-1}$, $\nu_{\text{Ru-O}} \sim 480 \text{ cm}^{-1}$ were observed in IR, showing their presence in compound^{48,49}.

$\text{Ru}3d_{3/2}$ photoelectron peak BE 284.8 eV was observed in $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ but it decreased $\sim \text{BE} = 282.6 \text{ eV}$ in complex $[\text{RuCl}_3 \text{L}^1\text{L}^2]$ suggesting electron density on ruthenium metal ion increased due to coordination. Cl 2p BE $\sim 201.2 \text{ eV}$ in $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ increased in $[\text{RuCl}_3 \text{L}^1\text{L}^2] \sim \text{BE} \sim 202.4 \text{ eV}$,

suggesting chlorine atom is coordinated with ruthenium metal ion⁵⁰. N1s photoelectron peak of L2 = Methionine or leucine or cysteine or serine or isoleucine ~BE in range of -

399.4eV, -399.8eV increased in $[\text{RuCl}_3 \text{ L}^1 \text{ L}^2]$ complexes. BE~401.6(eV) suggested nitrogen atom of methionine coordinated to $[\text{RuCl}_3 \text{ L}^1 \text{ L}^2]$ complexes⁵⁰.

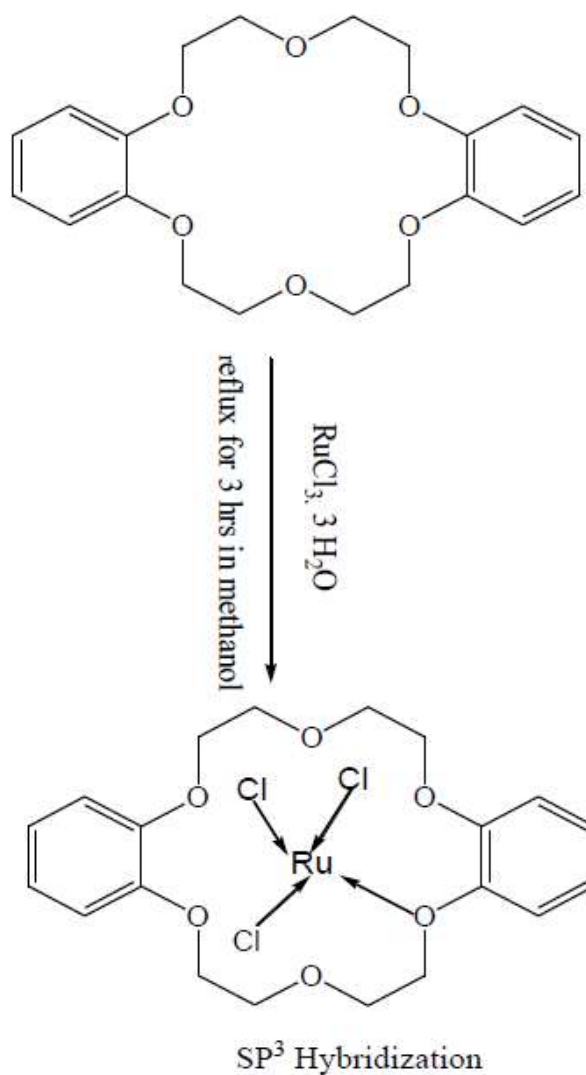
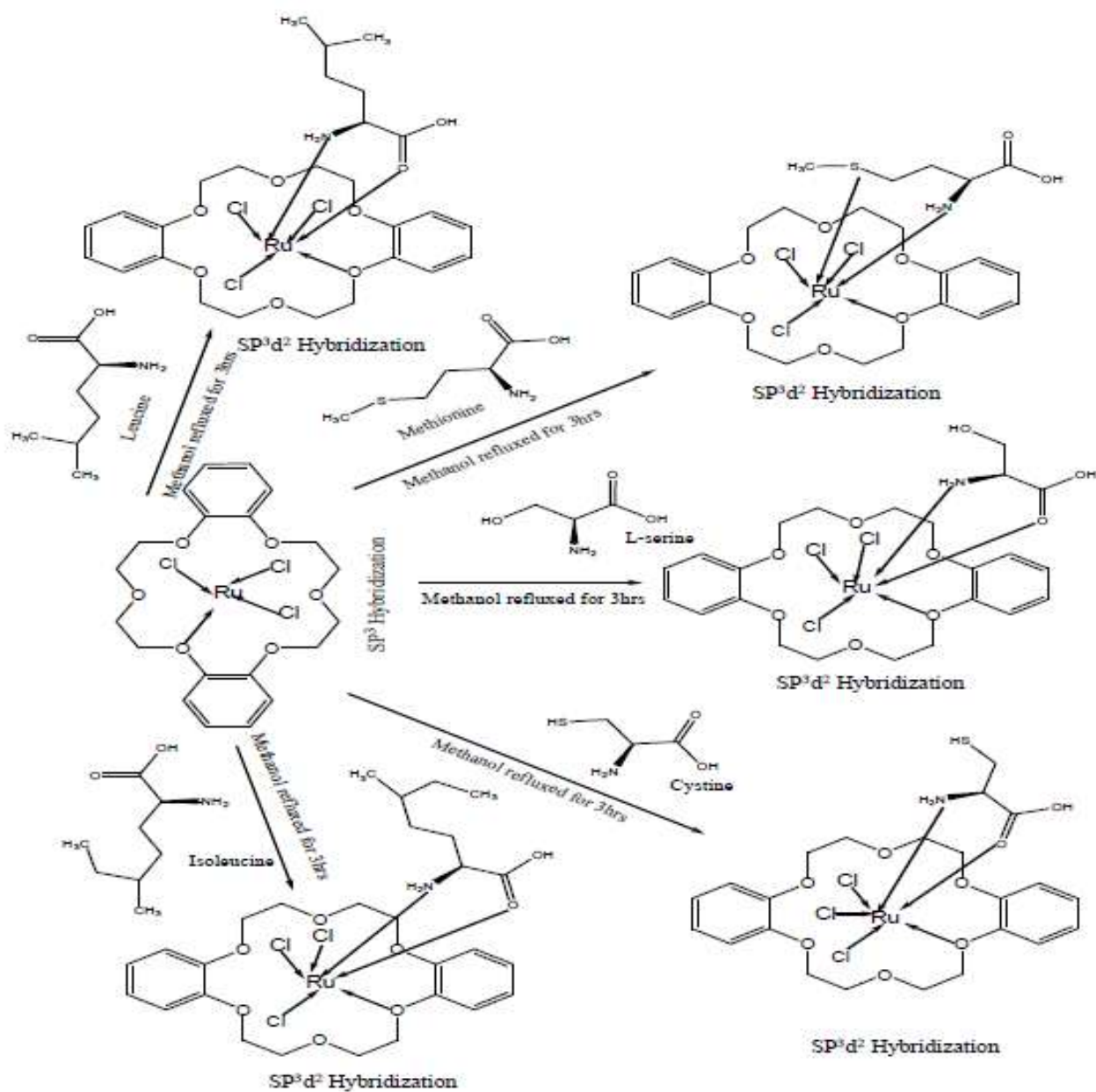


Fig. 1: Synthesis of $[\text{RuCl}_3 \text{ L}^1]$

Table I
Analytical data of $[\text{RuCl}_3 \text{ L}^1 \text{ L}^2]$ complexes

S. N.	Compounds	Elemental Analysis (%): Found (Calcd.)						Molar Conductance ($\text{Ohm}^{-1} \text{Cm}^2 \text{mol}^{-1}$)
		C	H	N	O	S	Cl	
1.	$\text{RuCl}_3(\text{DB18C6})(\text{Met})$	41.6 (41.8)	4.60 (4.62)	2.00 (1.95)	17.4 (17.8)	4.60 (4.47)	14.8 (14.8)	30
2.	$\text{RuCl}_3(\text{DB18C6})(\text{Leu})$	44.7 (44.6)	5.40 (5.35)	2.03 (2.00)	18.4 (18.3)	-	15.4 (15.2)	28
3.	$\text{RuCl}_3(\text{DB18C6})(\text{Cys})$	40.1 (40.1)	5.20 (4.54)	2.05 (2.03)	18.4 (18.5)	4.65 (4.70)	15.8 (15.4)	20
4.	$\text{RuCl}_3(\text{DB18C6})(\text{Iso-L})$	44.7 (44.6)	5.32 (5.34)	2.00 (2.00)	18.4 (18.3)	-	15.4 (15.2)	18
5.	$\text{RuCl}_3(\text{DB18C6})(\text{L-Ser})$	41.8 (41.5)	4.70 (4.64)	2.06 (2.08)	21.6 (21.4)	-	15.4 (15.8)	22

Fig. 2: Synthesis of $[RuCl_3L^1L^2]$ Table II
 $Ru_{3d_{3/2}}$, N1s, Cl2p, S2p and O1s binding Energies(eV)

S.N.	Compound	$Ru_{3d_{3/2}}$	Cl2p	N1s	S2p	O1s
1.	$RuCl_3 \cdot 3H_2O$	284.8	201.2	-	-	-
2.	Dibenzo- 18-crown-6	-	-	-	-	531.2
3.	methionine	-	-	399.4	145.2	-
4.	leucine	-	-	399.6	-	531.4
5.	cysteine	-	-	399.4	-	531.4
6.	serine	-	-	399.6	-	531.4
7.	isoleucine	-	-	399.8	-	531.4
8.	$[RuCl_3L^1L^2]$	282.6	202.4	401.6	146.2	531.4(Uncord) 532.4(Coord)

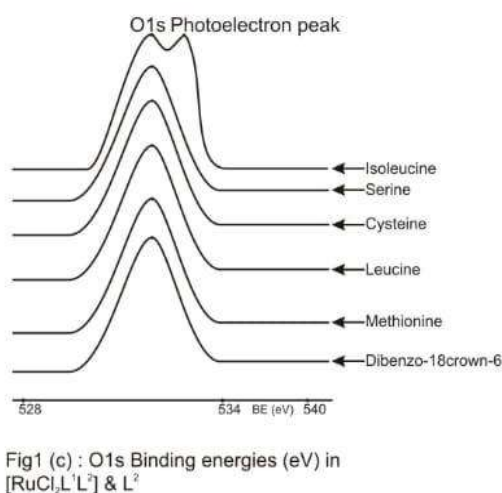
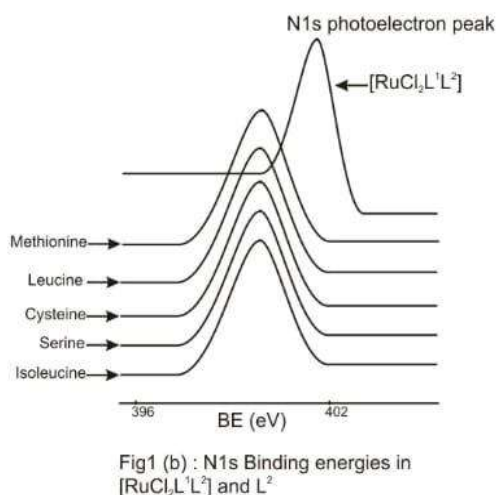
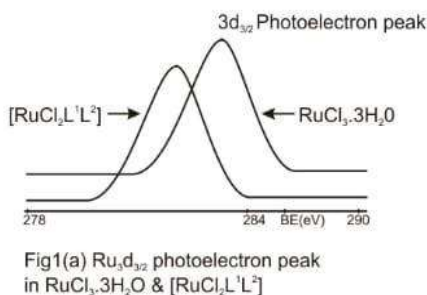


Fig. 3: XPS Spectra of $Ru_{3d_{3/2}}$ and N1s and O1s

S2p photoelectron peak in methionine $\sim BE-145.2eV$ increased in $[RuCl_3 L^1L^2]$. BE $\sim 146.2eV$ – suggested coordination of sulphur atom of methionine in $[RuCl_3 L^1L^2]$ complex.⁵⁰ In $[RuCl_3 L^1L^2]$ complex two O1s peaks were observed- one coordinated and other uncoordinated.

Conclusion

On the basis of elemental analysis, molar conductance data showing of all these molecular adducts suggested that all are nonionic and IR and X-ray photoelectron spectra (XPS) results shown in figure 3 suggested structure of these

prepared molecular adducts as assigned and an octahedral geometry was established.

Acknowledgement

One of the authors (RK) is thankful to Department of Chemistry, University of Allahabad and University Grants Commission for providing financial assistance. This study is part of Mr. Rahul Kanaoujiya, Ph.D. thesis.

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(Received 11th December 2020, accepted 21st January 2021)