

Application of Halides Complexes of Ruthenium (II) in Metallopharmaceuticals and in Material Science: Part-I

Vishnu Kumar Sahu^{1,*}, Anil Kumar Soni², Kavindra Kumar Mishra³, Rajesh Kumar Singh¹

¹Department of Chemistry, Maharani Lal Kunwari Post Graduate College, Tulsipur Road, Balrampur-271201(U.P.), India

²Department of Chemistry, Shia P.G. College, Sitapur Road, Lucknow-206020 (U.P.), India

³Department of Physics, Faculty of Science & Technology, Mewar University, Gangrar, Chittorgarh, Rajasthan, India

*Correspondence should be addressed to Vishnu Kumar Sahu, vishnukr_sahu@rediffmail.com

Received date: March 21, 2023, **Accepted date:** April 12, 2023

Citation: Sahu VK, Soni AK, Mishra KK, Singh RK. Application of Halides Complexes of Ruthenium (II) in Metallopharmaceuticals and in Material Science: Part-I. Arch Pharmacol Ther. 2023;5(1):25-35.

Copyright: © 2023 Sahu VK, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

Abstract

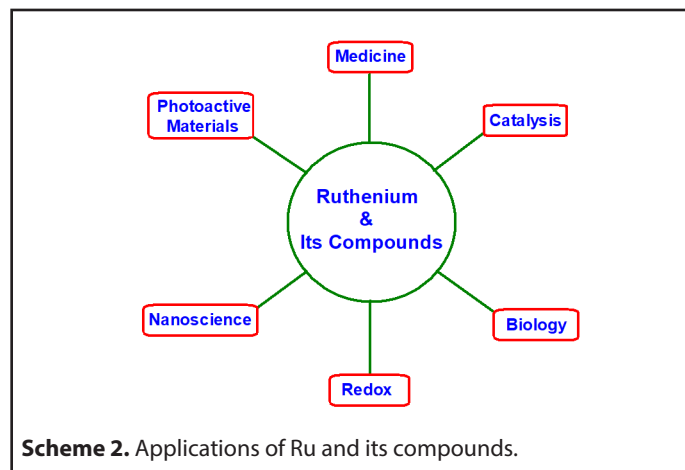
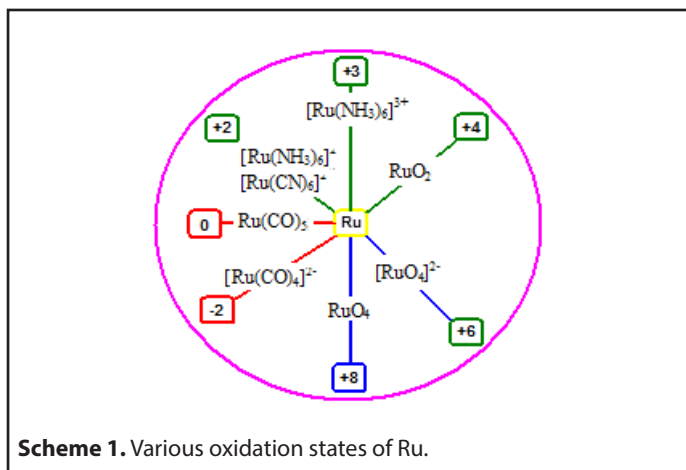
Ruthenium readily forms coordinate-complexes and these complexes have their applications in diverse fields. A survey of literature shows that designing of new ligands that can be complexed with Ruthenium (Ru) in various oxidation states can lead to development of new materials with diverse applications. In 21st century the gravity of approach of material science together with computer science has shifted from, how to make a molecule to what molecule to make, in other words molecular design. And now these are also quantized. As we know that physics, chemistry, and biology were explored at atomic levels and finally mathematical data were fed to grow required software for aimed simulations. The aim of present study is to study halides and mixed halides of Ru(II), which more precisely can help in the development of new Ru(II) complexes of desired application and or can help in fine tuning the property of pre-existing Ru(II) complexes. Thus, this study of atomistic details of halides of Ru(II) compounds along with construction of molecular orbital diagram at a glance will provide an insight of physicochemical, biochemical, electrochemical, thermochemical, magnetic, spectrochemical, catalytic, photoactive, and materialistic details. And this will help to solve the difficulties of synthesis of various complexes yet not synthesized. We know that all chemical reaction of complex compounds will be affected firstly by availability of vacant orbital(s) on metal ion (Ru²⁺) and secondly by the easiness of donation of electron pair(s) by ligands as we have also studied cloud-expanding effect, nephelauxetic effect, and electrochemical series of these Ruthenium(II) halides. The substitution reaction of complex compounds will also be mechanized and new substitution products (compounds) can also be prepared as topological analysis have also been made, those yet cannot synthesize by ordinary methods in required time and required cost too. Hence the halides of Ru(II) studied firstly. With the help of results of these studies, we will able to study complexation of these halides with selective ligands to form selective complex compounds of Ru(II) yet not prepared or have difficulties in preparation.

Keywords: Halides and mixed halides of Ru(II), sd-hybridization, MO diagram, EHT, PM3

Introduction

The ability of Ru to exist in many oxidation states is an important property of this element which plays an important role in its applications [1]. Ru forms compounds in -2, 0, +2, +3, +4, +6, and +8 oxidation states. -2 and 0 oxidation states are unusual oxidation states (**Scheme 1**). Day-to-day expanding in the chemistry of Ruthenium and its complexes is due to their applications directly or indirectly pre-requisite for many of today's problems related to anticancer drugs [2-8], polymers [9], materials science [6,8], and nanoscience [6,10-12] (**Scheme 2**). This is due to its versatile electron-transfer

pathways [13-18]. Survey of literature shows that ruthenium and its compounds now used: in solar cells [19,20], as catalyst [2,3,7-23], as determination of calcitonin level in blood [6], in Eleecys folate RBC assay to estimate folate deficiency in RBC [6], as immunosuppressant [6], as antimicrobial agents [24], as antibiotic agents [25], as inhibitors to inhibit over production of nitric oxide in biological cell [2,3], as metallopharmaceuticals in treatment of various diseases including cancer [2,3], radio sensitizers complexes with ruthenium are used in radiation therapy, as anti-metastasis drugs [2-8]. Dragutan et al. in editorial special issue review wrote "The valorization of Ru complexes in photochemistry and agrochemicals will



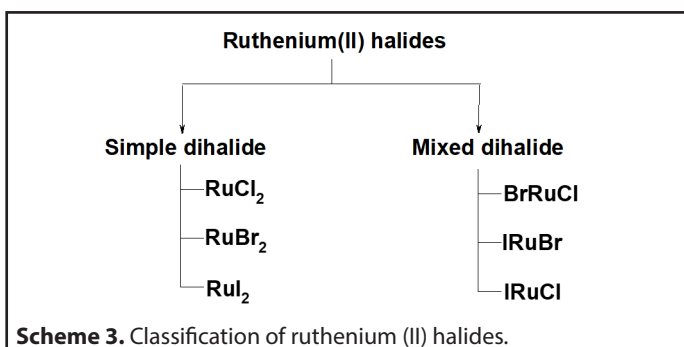
undoubtedly be forthcoming" [26]. Various complexes of Ru(II) with their various applications are described here. Poursharifi et al. have their focus on encapsulating Ruthenium-based carriers of nanosized structures or adduct with various macro biomolecules to generate efficacious anti-cancer therapies [6]. Ruthenium based complex compounds have also been used as drugs to activate or help to generate redox reactions [13-17]. As most of the Ruthenium complexes are less toxic than their Platinum counter parts, this offers development of Ruthenium-based anticancer drugs. (imidazole-H)[*trans*-RuCl₄(dmsO-5)(imidazole)] has entered onto phase-I clinical trial and showed anti-cancer activity against solid tumor metastasis [27]. Some bidentate N-donor or arene ligands, when complexed with Ru(II) have also been found to show significant anti-cancer activities [2-8]. Ruthenium(II) complex, "[Ru(*t*Bu₂byp)₂-(2-appt)](PF₆)₂" has been shown to exhibit moderate cytotoxicity towards several established various human cancer cells [21]. Sun et al. [4] examined nucleotide binding properties and cytotoxicity of several ruthenium(II) complexes with quinonediimine as auxiliary ligand. Ruthenium(II) complexed with ligand 9,10-phenanthroquinonediimine has highest DNA binding constant attributed due to its flat and large surface area, which provide a geometry that permits sizeable overlap with DNA base pairs. It has mild cytotoxicity with 50% inhibitory concentration of ~200 μM against carcinoma cell lines. The cell growth inhibition activity of complex [Cl(terpy)(tmphen)Ru]⁺ is due its binding affinity towards purines sites of nucleotides of DNA, and this depends upon chloride ligand. Binding of the *trans*-[Cl₄(Im)₂Ru]⁻ to apotransferrin for its anti-tumor activity takes several hours, but its Ind-derivatives, *trans*-[Cl₄(Ind)₂Ru]⁻ showed very fast action in few minutes. To kill the undesired cells in the body using N-heterocyclic ligands complexed with Ru(II) has also been reported in literatures. This photodynamic therapy (PDT) activity of agents depends on their ability to associate with biopolymers or cell membranes or DNA [28]. The radiophysical properties of ⁹⁷Ru are nearly ideal for some type of radiodiagnostic imaging [8]. Ruthenium-oxo oxalato cluster Na₇[Ru₄(μ-O)₄(C₂O₄)₆] exhibited promising anti-HIV-1 activity over 98% inhibition [8]. The IC₅₀ of this compound to reduce the catalytic activity of reverse transcriptase enzyme of human immunodeficiency virus-1

in nanomolar is 1.9 as reported by Sun et al. [4]. This activity of this compound is ten times more than the most used drug 3'-azido-3'-deoxythymidine-5'-triphosphate (AZT-TP) whose, IC₅₀ in nanomolar is 68. Further, this compound was able to show only antiviral activity instead of killing the host cells [4,5]. Anti-microbial activities in both bacterial and fungal cells of "octahedral polypyridyl ruthenium(III) complexes" were also reported by Yang et al. [24]. It is worthwhile mentioned that "octahedral ruthenium(II) complexes" have remarkable applications in Bio-medical sciences [24,25]. Early metathesis catalysis formed *in situ* from transition-metal halides has their limitation due to their high compression and lower easiness. Ruthenium based catalysts have remarkably high compression and lower easiness. In 1960s first catalytic activity of Ru based complex has been reported in literature and this was due to the RuCl₃(H₂O)_n metathesis. The catalysis of "areneruthenium(II) complexes" ranges from hydrogen transfer to ring-closing. García-Peña et al., have made solventless synthesis of Ru nanoparticles along with the use of polyphosphorhydrazone dendrons as coatings leads to Ru nanoparticles in zero oxidation state which are air stable, and proved to be very good nanomaterials for hydrogenation catalysis [9]. Santoro et al., have developed tris(1,10-phenantroline)ruthenium(II) (Ru(phen)₃)⁺² as a thermometer of nanosized doped with nanosized silica, applicable to monitor the temperature of membrane surfaces in real membrane process [11,12]. These workers also developed nanoparticles that have application for high photochemical and strong phosphorescence activity with respect to Ru(phen)₃⁺². Millett and Durham have developed a new method to study intracomplex electron transfer that utilizes a photoactive tris(bispyridine)ruthenium group [Ru(II)] which was covalently attached to a protein (cytochrome c) [18]. Application of ruthenium based sensitizers having thiocyanate and other ligands have been reviewed by Qin and Peng for dye-sensitized solar cells (DSSCs), among them several sensitizers have 10% more efficiency with respect to available sensitizers [18-20]. The aim of present study is to study the atomic and sub-atomic i.e., electronic structure of ruthenium(II) halides by evaluating eigenvalues, eigenvector, and overlap matrix of molecular orbitals [29-32]. During the study, three objectives arose: (i) to draw the 3D structure

of all the compounds and to optimize their geometry (ii) to evaluate the eigenvector, overlap matrix, and eigenvalues of the compounds and (iii) build up molecular orbital diagram of compounds that at a glance provides clear cut electronic picture of the molecule, which more precisely can explain or help to explain the various properties of the molecule. The basic picture of these halides help to achieve the goal for other complexes of Ru(II) those are vital for the society. A survey of literature also shows that designing of new ligands that can be complexed with ruthenium in different oxidation states can lead to development of new materials. For new materials of diverse applications there is and will be a continuous step-by-step study to discover new ligands and their new ruthenium complexes. Newly designed complex compounds can be synthesized from their halides or by substitution reactions from known complex compounds.

Material and Methods

The study material are ruthenium(II) halides. These halides have been classified in to two groups: simple ruthenium dihalides and mixed dihalides (**Scheme 3**). Three simple



ruthenium dihalides exist. These are ruthenium(II) chloride, ruthenium(II) bromide and ruthenium(II) iodide, except ruthenium(II) fluoride which does not exist. Three ruthenium mixed dihalides are also possible. These are Br–Ru–Cl, I–Ru–Br, and I–Ru–Cl. The adopted methods for various calculations of ruthenium dihalides are based on Mulliken's population analysis [23]. Mulliken defined ϕ_i (molecular orbital), $n_{r,i}$ (the contributions of electrons in each occupied MO) and $n_{r-s,i}$ (overlap population that explain bonding, antibonding and nonbonding nature of bond), as below:

$$\phi_i = \sum_{rk} c_{irk} \chi_{rk} \quad \text{Eq.1}$$

$$n_{r,i} = n_i c_{ri}^2 \quad \text{Eq.2}$$

$$n_{r-s,i} = n_i (2c_{ri} c_{si} S_{rs}) \quad \text{Eq.3}$$

here n_i is the number of electron in ϕ_i , $i = 1-17$, c_{ri} is the coefficient of atomic orbitals for Ru-atom, c_{si} is the coefficient of AOs for other atom (Cl-2 or Cl-3) and S_{rs} is the overlap integral between the two AOs (one of an atom Ru-1 or Cl-2 and one of another atom Cl-2 or Cl-3). In order to obtain minimum energy structure, we optimized the geometry of each halide by opting Extended Hückel Theory (EHT). All the calculations were performed on CAChe software [33,34]. From minimum energy structure we have extracted values of eigenvectors, overlap matrix, and eigenvalues. By submitting the values of eigenvector and overlap matrix in eqn.3, we have derived the values of overlap population and tabulated in **Tables 1 and 2** for halides and mixed dihalides, respectively. And the summation of values of overlap population was obtained to describe bonding, nonbonding,

Table 1. Quantitative and qualitative nature of occupied molecular orbitals of ruthenium dihalides.

MO No.	RuCl ₂			RuBr ₂			RuI ₂		
	$\Sigma n_{r-s,i}$	sign	MOs	$\Sigma n_{r-s,i}$	sign	MOs	$\Sigma n_{r-s,i}$	sign	MOs
ϕ_1	0.1924	+	BMO	0.2091	+	BMO	0.3042	+	BMO
ϕ_2	0.1237	+	BMO	0.1371	+	BMO	0.1742	+	BMO
ϕ_3	0.4502	+	BMO	0.2487	+	BMO	0.0936	+	BMO
ϕ_4	0.2226	+	BMO	0.1395	+	BMO	0.0936	+	BMO
ϕ_5	0.2228	+	BMO	0.1395	+	BMO	0.1248	+	BMO
ϕ_6	0.0000	0	NBO	0.0000	0	NBO	0.0000	0	NBO
ϕ_7	0.0000	0	NBO	0.0000	0	NBO	0.0000	0	NBO
ϕ_8	0.2853	+	BMO	0.3256	+	BMO	0.3359	+	BMO
ϕ_9	0.1182	+	BMO	0.0941	+	BMO	0.1849	+	BMO
ϕ_{10}	0.1202	+	BMO	0.0940	+	BMO	0.0783	+	BMO
ϕ_{11}	0.0735	+	BMO	0.1433	+	BMO	0.0783	+	BMO

MOs is molecular orbitals, BMO is bonding molecular orbital, ABMO is antibonding molecular orbital, and NBO is nonbonding molecular orbitals

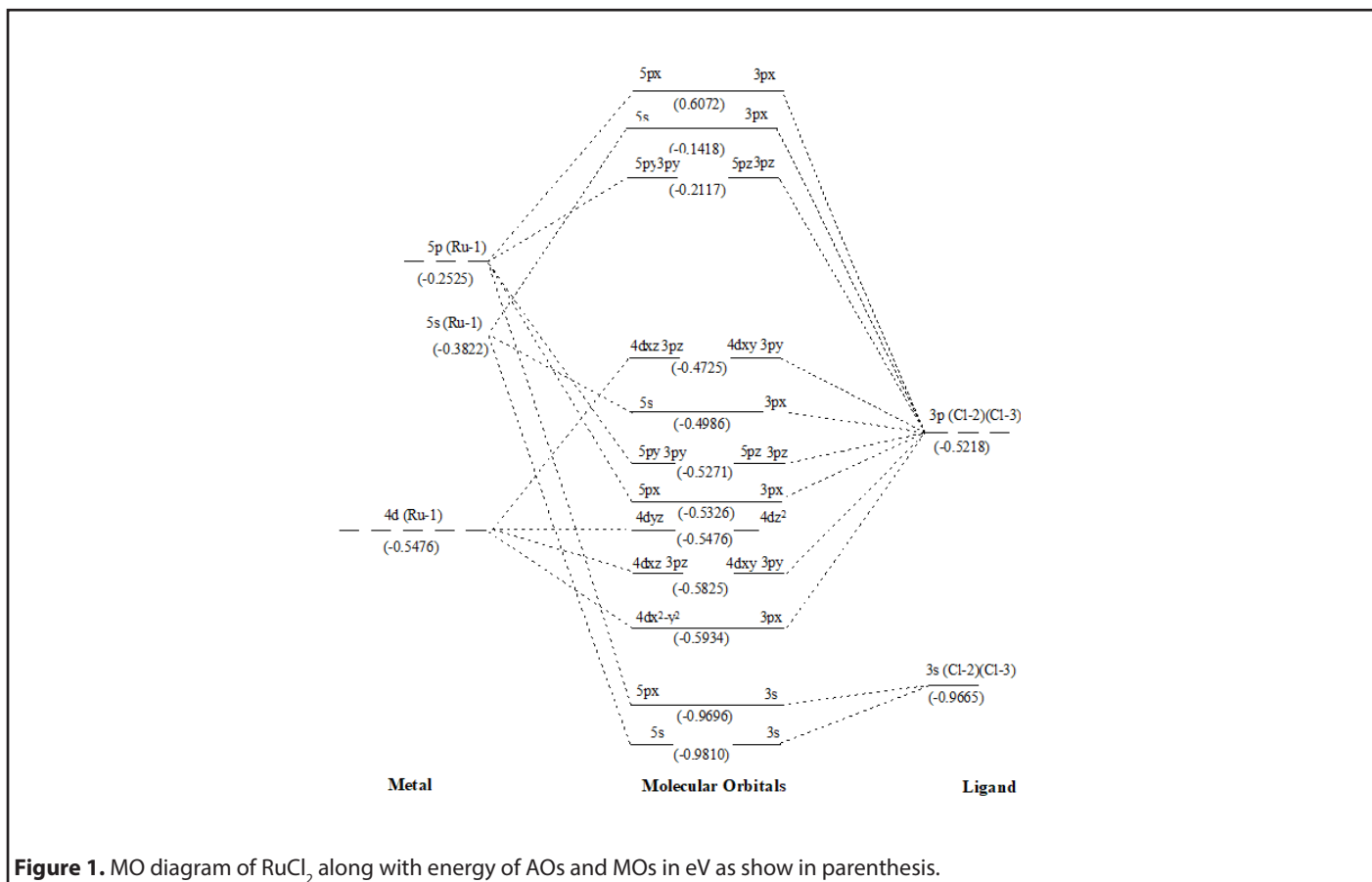
Table 2. Quantitative and qualitative nature of occupied molecular orbitals of ruthenium mixed dihalides.

MO No.	Ru(II)BrCl			Ru(II)IBr			Ru(II)ICl		
	$\Sigma n_{r-s,i}$	sign	MOs	$\Sigma n_{r-s,i}$	sign	MOs	$\Sigma n_{r-s,i}$	sign	MOs
Φ_1	0.1604	+	BMO	0.1358	+	BMO	0.1585	+	BMO
Φ_2	0.1719	+	BMO	0.2496	+	BMO	0.2527	+	BMO
Φ_3	0.3051	+	BMO	0.2372	+	BMO	0.2523	+	BMO
Φ_4	0.1949	+	BMO	0.1442	+	BMO	0.1848	+	BMO
Φ_5	0.1949	+	BMO	0.1471	+	BMO	0.1848	+	BMO
Φ_6	0.0000	0	NBO	0.0000	0	NBO	0.0000	0	NBO
Φ_7	0.0000	0	NBO	0.0000	0	NBO	0.0000	0	NBO
Φ_8	0.2422	+	BMO	0.1698	+	BMO	0.1824	+	BMO
Φ_9	0.0504	+	BMO	0.0064	+	BMO	-0.0105	-	ABMO
Φ_{10}	0.0495	+	BMO	0.0063	+	BMO	-0.0105	-	ABMO
Φ_{11}	0.1626	+	BMO	0.2292	+	BMO	0.2270	+	BMO

MOs is molecular orbitals, BMO is bonding molecular orbital, ABMO is antibonding molecular orbital and NBO is nonbonding molecular orbitals

and antibonding molecular orbitals have also been presented in these tables, respectively. After that using all above along with eigenvalues, molecular orbital diagram has been drawn (Figures 1-6). Finally topological data have been extracted to

describe the feasibility of the breaking and making old and new bond formation, respectively. Before all these, we have also examined the nature and contribution of atomic orbitals and then their mixing (valence bond theory) or overlapping



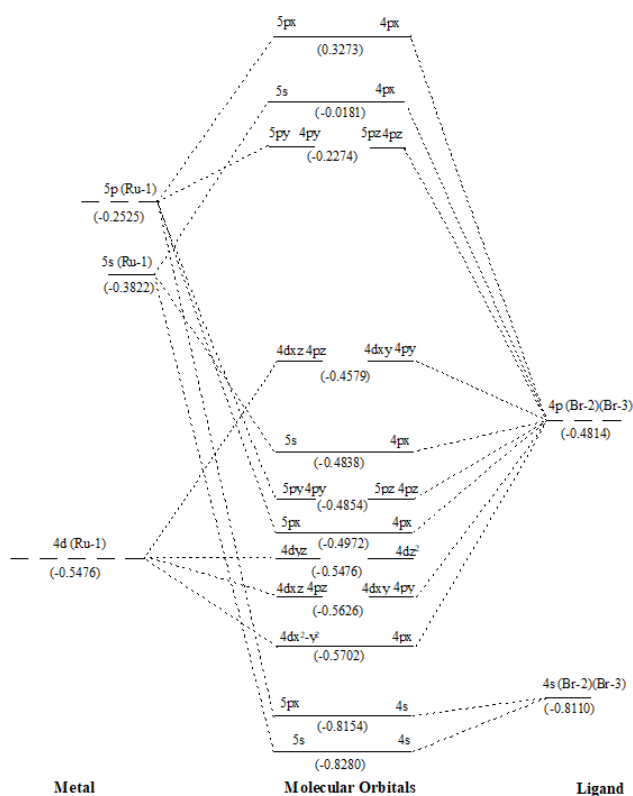


Figure 2. MO diagram of RuBr₂ along with energy of AOs and MOs in eV as show in parenthesis.

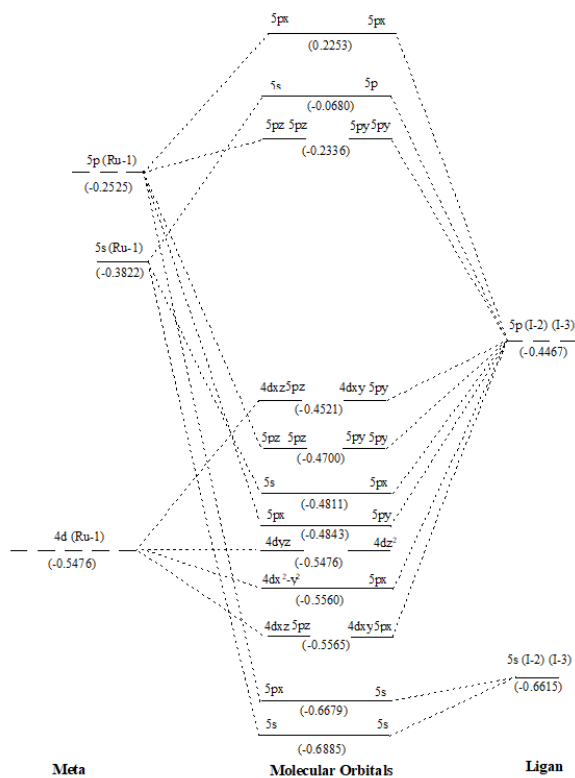


Figure 3. MO diagram of RuI₂ along with energy of AOs and MOs in eV as show in parenthesis.

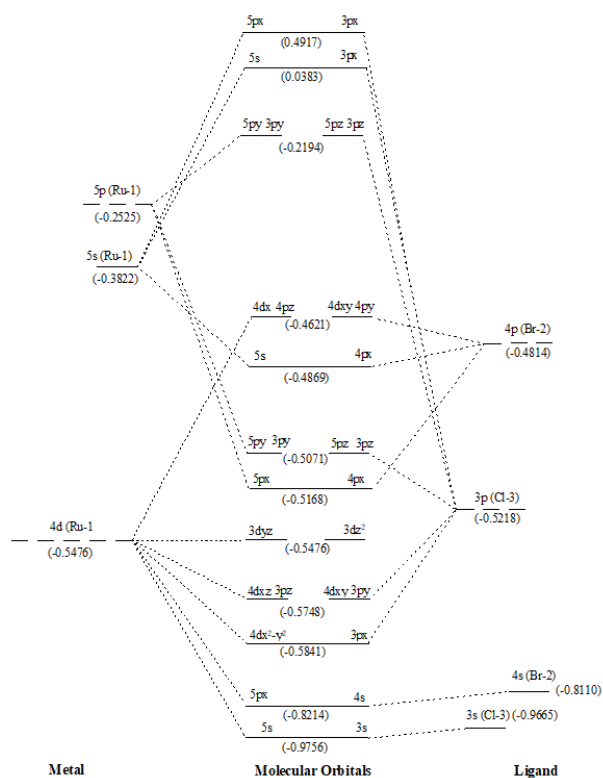


Figure 4. MO diagram of Ru(II)BrCl along with energy of AOs and MOs in eV as show in parenthesis.

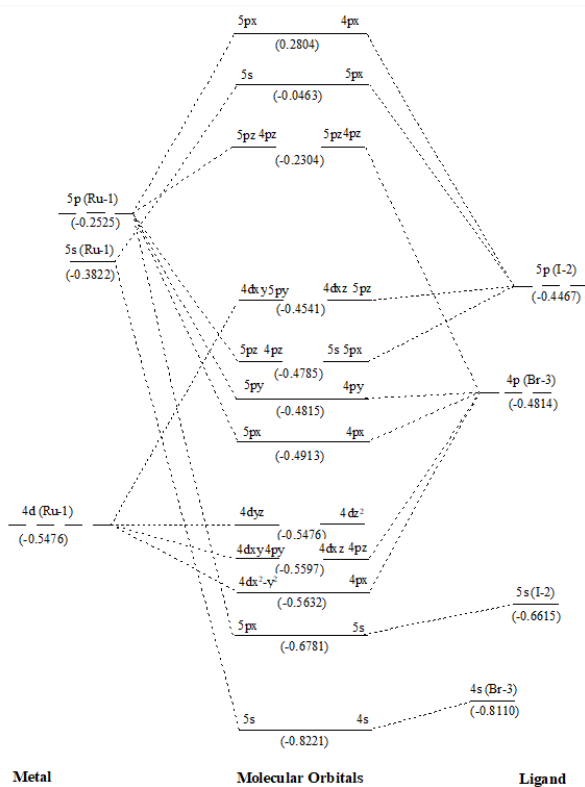
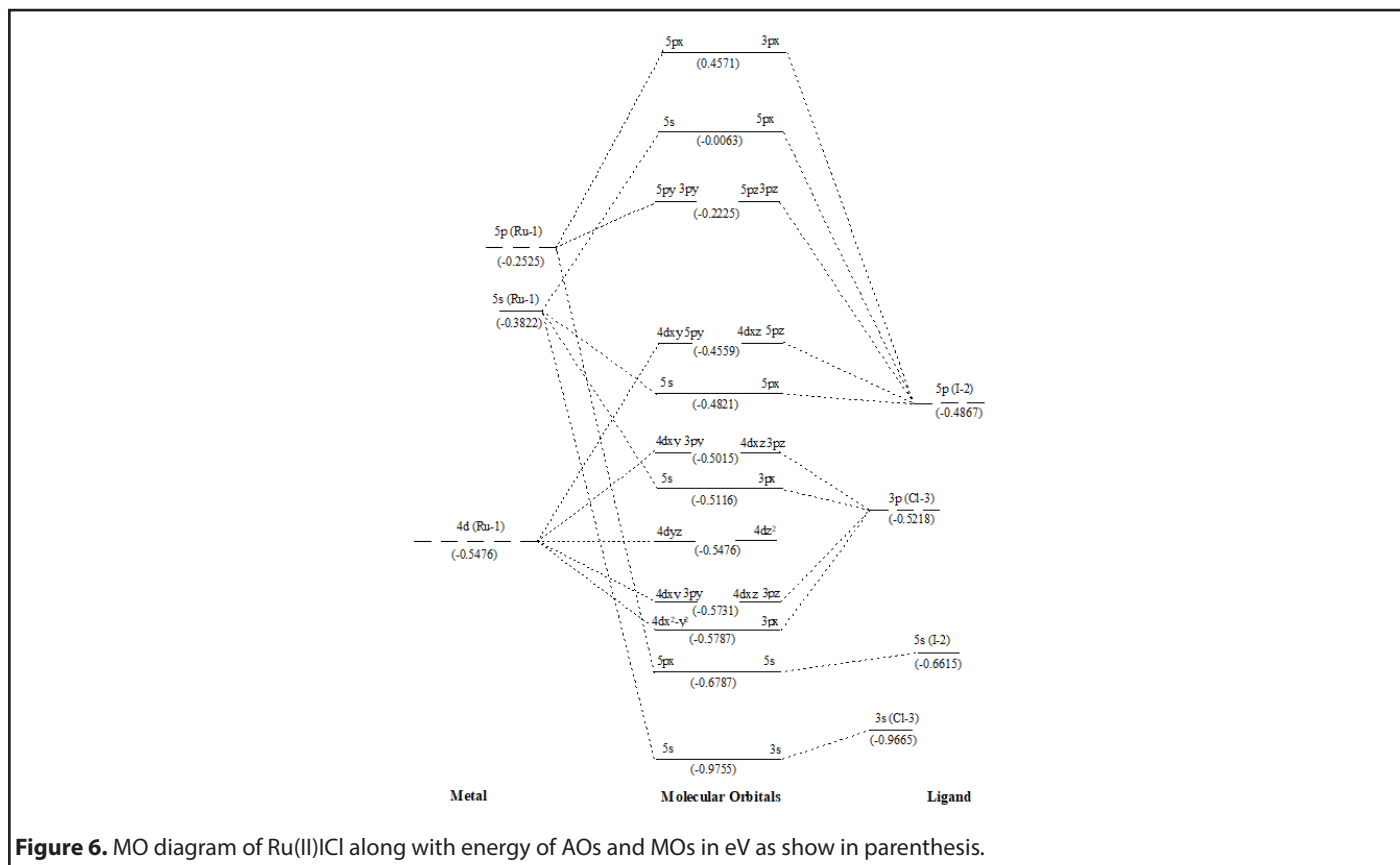


Figure 5. MO diagram of Ru(II)IBr along with energy of AOs and MOs in eV as show in parenthesis.



(molecular orbital theory). V.B. Theory and M.O. theory on their refinements gave same wave function for the molecule but they differ in their approximations only. Mulliken (1955) also correlated the bonded interaction of V.B.T. with positive overlap population and non-bonded repulsion of V.B.T. with negative population analysis [29-32].

Result and Discussion

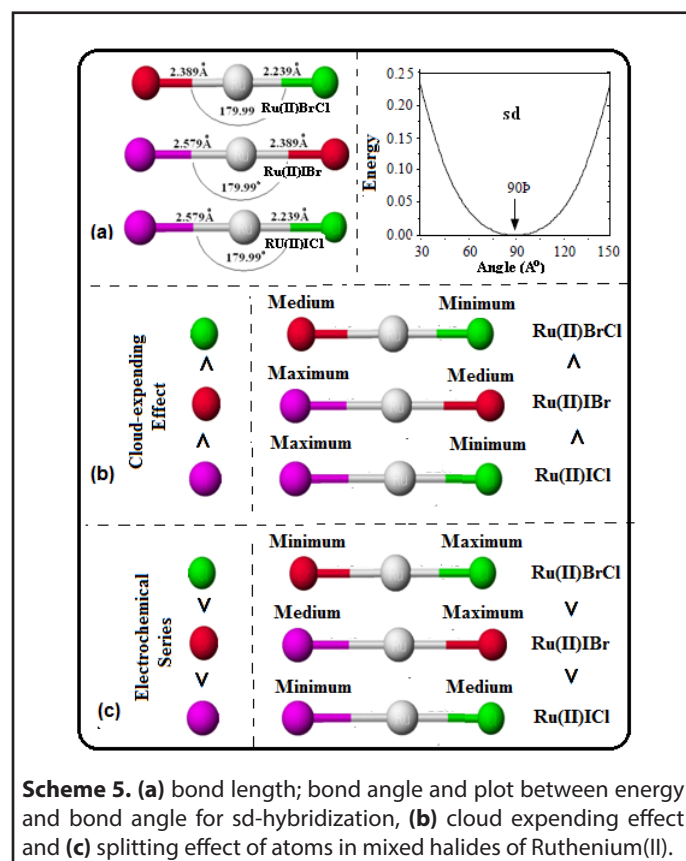
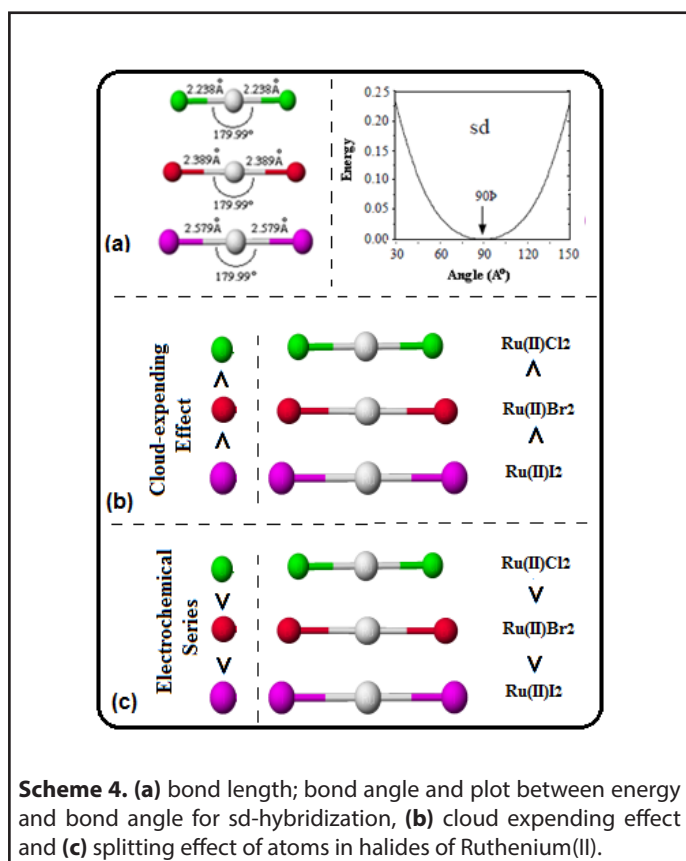
It was Landis, who discovered sd^n -hybridization ($n = 1$ to 5) along with molecular shape and bond angles in his seminal publications [35-37]. Further, he also explained co-relationship between sd^n -hybridization and its bond angle by plotting a graph between energy and bond angle. In order to explore atomic orbitals detail with respect to hybridization, we have

examined the contribution of 4d, 5s, and 5p AOs of Ru-1 in RuX₂. For this only occupied MO ($\varphi_1 - \varphi_{11}$) were considered. And values of c_i of each χ of 5s, 5px, 5py, 5pz, 4dx²-y², 4dxy, 4xz of above eleven molecular orbitals were added and the results were tabulated in **Table 3**. Analysis of this table reflected that major contributions are from orbitals of 4d and 5s. Among 4d-orbitals the contribution is: 4dx²-y² > 4dxz > 4dxy. The negligible contribution of 5s-orbital has disclosed sd -hybridization (**Schemes 4a and 5a**).

Further, we know that nephelauxetic series for a given metal ion are: F⁻ < H₂O < NH₃ < en < ox < SCN⁻ < Cl⁻ < CN⁻ < Br⁻ < I⁻ [38]. To explain cloud expending effect of these halides, we have made summation of values of $n_{r-s,i}$ and the results were also sketched and presented in **Scheme 3b and 4b**

Table 3. Summation values of various AOs of halides of Ru(II).

AO	Ru(II)Cl ₂	Ru(II)Br ₂	Ru(II)I ₂	Ru(II)BrCl	Ru(II)IBr	Ru(II)ICl
$\Sigma 4dx^2-y^2$	1.8387	1.9165	2.0004	2.4501	4.9002	9.8004
$\Sigma 4dxy$	1.0407	1.1820	1.2399	2.1893	4.3786	8.7572
$\Sigma 4dxz$	0.8364	0.9694	1.0145	2.1527	4.3054	8.2407
$\Sigma 5s$	0.6598	0.6635	0.6742	1.1012	2.2024	4.4047
$\Sigma 5px$	0.2471	0.2921	0.3385	0.7407	1.4814	2.8401
$\Sigma 5py$	0.1477	0.1494	0.1498	0.6454	1.2908	2.5816
$\Sigma 5pz$	0.1276	0.1254	0.1218	0.3866	0.7732	1.5464



(ruthenium halides and ruthenium mixed dihalides). In case of normal ruthenium dihalides the sequence is $RuI_2 > RuBr_2 > RuCl_2$, which is in accordance to nephelauxetic series i.e. the effective positive charge on Ru(II) is reduced greater by iodide and lesser by chloride (**Scheme 4b**). In mixed dihalides the sequence is $I-Ru-Cl$ ($\Delta\chi_{Cl-Cl} = 0.5$) $>$ $I-Ru-Br$ ($\Delta\chi_{I-Br} = 0.3$) $>$ $Cl-Ru-Br$ ($\Delta\chi_{Cl-Br} = 0.2$). Here, the difference in electronegativity ($\Delta\chi$) between X_1 and X_2 ($X = Cl, Br, I$) were used to explain the cloud-expanding effect. Higher the value of $\Delta\chi$ greater will be the cloud-expanding effect (**Scheme 5b**).

After that values of overlap population of eleven MOs of RuX_2 and $RuXX'$ have also been added ($\sum n_{r-s,i}$) (**Tables 1 and 2**) to get a precise description of quantitative as well as qualitative nature of molecular orbitals and participating atomic orbitals. And the molecular orbital diagrams have also been constructed by using data of these tables along with eigenvalues. These values are also shown in parenthesis of the MO diagrams i.e. **Figures 1 to 6**. The AOs of respective atom involving in LCAOs are shown with their energy (in eV) and also the type of orbital combination that results in corresponding MOs (σ BMOs, π BMOs, σ ABMOs, π ABMOs, and NBOs). These diagrams at a glance provide very deep insight of the halides of Ru(II) in atomistic levels with LCAOs details. **Table 1** also reflected that among the eleven molecular orbitals, nine are BMO (φ_1 - φ_5 and φ_8 - φ_{11}) and two are NBO (φ_6 and φ_7) in simple ruthenium dihalides. In mixed dihalides as reflected by **Table 2** that among the eleven molecular orbitals, nine are BMO (φ_1 -

φ_5 and φ_8 - φ_{11}) and two NBO (φ_6 and φ_7) in Ru(II)BrCl as well as in Ru(II)IBr. While in Ru(II)ICl, among the eleven molecular orbital, seven are BMO (φ_1 - φ_5 , φ_8 and φ_{11}), two are NBO (φ_6 and φ_7) and two are ABMO (φ_9 and φ_{10}). A close look on **Schemes 6 and 7**, each of which explore magnitude of splitting of metal d-orbital in ruthenium(II) halide and mixed dihalides respectively, reflected the trends: $RuCl_2 > RuBr_2 > RuI_2$ and $Ru(II)ICl > Ru(II)BrCl > Ru(II)IBr$. These are also in accordance with electrochemical series [39].

The topology of these halides are also studied and presented in **Table 4**, and predicted that it is very difficult to replace Cl atom from $Cl-Ru-Cl$ ($\sum n_{r-s,i} = 1.8089$) to form $Br-Ru-Cl$. But, it can be easily prepared from $Br-Ru-Br$ ($\sum n_{r-s,i} = 1.5309$) by replacing one of its Br atoms by Cl atom through substitution reaction. Similarly, $I-Ru-Br$ can be prepared easily by replacing one of the $I-Ru-I$ ($\sum n_{r-s,i} = 1.4678$) by Br atom. And, $I-Ru-Cl$ can be prepared easily by replacing one of the $I-Ru-I$ ($\sum n_{r-s,i} = 1.4678$) by Cl atom than $Br-Ru-Br$. The study will be helpful in designing of new ligands that can form complexes with Ru in various oxidation states which can lead to development of new materials.

Conclusions

(i) The study well support the Landis concepts [35-37] of sd^n -hybridation (here $n = 1$) as bond angle and contributions of s-orbital and d-orbital of Ru(II) is maximum with negligible contribution of p-orbitals.

Scheme 6. Splitting of d orbitals in Ruthenium(II) halides.

Energy (eV)	Ru ⁺⁺	RuCl ₂	RuBr ₂	RuI ₂
-0.4521		4dxz, 4dxy		
-0.4579			4dxy, 4dxz	
-0.4725				4dxy, 4dxz
-0.5476	4dx ² -y ² , 4dz ² , 4dxy, 4dyz, 4dxz	4dyz, 4dz ²	4dyz, 4dz ²	4dyz, 4dz ²
-0.5560				4dx ² -y ²
-0.5702			4dx ² -y ²	
-0.5934		4dx ² -y ²		

Scheme 7. Splitting of d orbitals in Ruthenium(II) mixed dihalides.

Energy (eV)	Ru ⁺⁺	Ru(II)BrCl	Ru(II)IBr	Ru(II)ICl
-0.4541			4dxy, 4dxz	
-0.4559				4dxy, 4dxz
-0.4621		4dxz, 4dxy		
-0.5476	4dx ² -y ² , 4dz ² , 4dxy, 4dyz, 4dxz	4dyz, 4dz ²	4dyz, 4dz ²	4dyz, 4dz ²
-0.5632			4dx ² -y ²	
-0.5787				4dx ² -y ²
-0.5841		4dx ² -y ²		

Table 4. Summary of topology of Ruthenium(II) halides and mixed dihalides

Molecule	$\sum \sum n_{r-s,i}$	Bond	Length (Å)	Bond	Length (Å)	Bond Angle(°)
Cl–Ru–Cl	1.8089	Cl–Ru	2.238	Ru–Cl	2.238	179.99°
Br–Ru–Br	1.5309	Br–Ru	2.389	Ru–Br	2.389	179.99°
I–Ru–I	1.4678	I–Ru	2.579	Ru–I	2.579	179.99°
Br–Ru–Cl	1.5319	Br–Ru	2.389	Ru–Cl	2.239	179.99°
I–Ru–Br	1.3256	I–Ru	2.579	Ru–Br	2.389	179.99°
I–Ru–Cl	1.4215	I–Ru	2.579	Ru–I	2.239	179.99°

(ii) These halides also support the cloud-expanding effect with experimental data and also follow the nephelauxetic effect [38].

(iii) The results are also in agreement with spectrochemical series in connection with splitting effects [39].

(iv) This study of atomistic details of halides of Ru(II) compounds and construction of molecular orbital diagram that at a glance will provide an insight of physicochemical, biochemical, electrochemical, thermochemical, magnetic, spectrochemical, catalytic, photoactive, and materialistic details. And this will help to solve the difficulties of synthesis of various complexes yet not synthesized.

(v) Topological data as presented in **Table 4**, will describe the feasibility of substitution reactions of halogens with other

ligands to prepare various complexes yet not synthesized.

Acknowledgements

Authors are very thankful to Principal and Head of Department of Maharani Lal Kunwari Post Graduate College, Tulsipur Road, Balrampur-271201 (U.P.) for laboratory facilities.

The paper is dedicated to my teacher; mentor, guru father and eminent chemist – respected Prof. P.P. Singh (DSc., F.N.A.Sc.) also known as Doctor Sahab, Ex. Principal Maharani Lal Kunwari Post Graduate College, Tulsipur Road, Balrampur-271201 (U.P.), India.

References

1. Sahu AK, Dash DK, Mishra K, Mishra SP, Yadav R, Kashyap P.

- Properties and applications of ruthenium. In: Noble and Precious Metals-Properties, Nanoscale Effects and Applications. 2018 Jul 4. IntechOpen.
- Clarke MJ. Ruthenium metallopharmaceuticals. Coordination Chemistry Reviews. 2002 Oct 1;232(1-2):69-93.
 - Clark MJ. Ruthenium metallopharmaceuticals. Coordination Chemistry Reviews. 2003 Jan;236(1-2):209-33.
 - Sun RW, Ma DL, Wong EL, Che CM. Some uses of transition metal complexes as anti-cancer and anti-HIV agents. Dalton Transactions. 2007(43):4884-92.
 - Hill CL, Weeks MS, Schinazi RF. Anti-HIV-1 activity, toxicity, and stability studies of representative structural families of polyoxometalates. Journal of Medicinal Chemistry. 1990 Oct;33(10):2767-72.
 - Poursharifi M, Wlodarczyk MT, Mieszawska AJ. Nano-based systems and biomacromolecules as carriers for metallodrugs in anticancer therapy. Inorganics. 2018 Dec 20;7(1):2.
 - Keeppler BK (Ed.) Metal Complexes in Cancer Chemotherapy. Weinheim, Germany: VCH; 1993. pp187-202.
 - Srivastava SC, Mausner LF, Clarke MJ. Radioruthenium-labeled compounds for diagnostic tumor imaging. In: Ruthenium and Other Non-Platinum Metal Complexes in Cancer Chemotherapy. Berlin Heidelberg: Springer; 1989. pp. 111-149.
 - García-Peña NG, Caminade AM, Ouali A, Redón R, Turrin CO. Solventless synthesis of Ru (0) composites stabilized with polyphosphorhydrazone (PPH) dendrons and their use in catalysis. RSC advances. 2016;6(69):64557-67.
 - Hudson R, Chazelle V, Bateman M, Roy R, Li CJ, Moores A. Sustainable synthesis of magnetic ruthenium-coated iron nanoparticles and application in the catalytic transfer hydrogenation of ketones. ACS Sustainable Chemistry & Engineering. 2015 May 4;3(5):814-20.
 - Santoro S, Sebastian V, Moro AJ, Portugal CA, Lima JC, Coelho IM, et al. Development of fluorescent thermoresponsive nanoparticles for temperature monitoring on membrane surfaces. Journal of Colloid and Interface Science. 2017 Jan 15;486:144-52.
 - Krause RA. Synthesis of ruthenium (II) complexes of aromatic chelating heterocycles: Towards the design of luminescent compounds. In: Coordination Compounds: Synthesis and Medical Application 2005 Mar 2 (pp. 1-52). Berlin, Heidelberg: Springer Berlin Heidelberg.
 - Casimiro DR, Richards JH, Winkler JR, Gray HB. Electron transfer in ruthenium-modified cytochromes c. sigma-tunneling pathways through aromatic residues. The Journal of Physical Chemistry. 1993 Dec;97(50):13073-7.
 - Rillema DP, Allen G, Meyer TJ, Conrad D. Redox properties of ruthenium (II) tris chelate complexes containing the ligands 2, 2'-bipyrazine, 2, 2'-bipyridine, and 2, 2'-bipyrimidine. Inorganic Chemistry. 1983 May;22(11):1617-22.
 - Prier CK, Rankic DA, MacMillan DW. Visible light photoredox catalysis with transition metal complexes: applications in organic synthesis. Chemical Reviews. 2013 Jul 10;113(7):5322-63.
 - Tfouni E. Photochemical reactions of amminoruthenium (III) complexes. Coordination Chemistry Reviews. 2000 Jan 1;196(1):281-305.
 - Wolfgang S, Streckas TC, Gafney HD, Krause RA, Krause K. Spectral and photophysical properties of ruthenium (II) 2-(phenylazo) pyridine complexes. Inorganic Chemistry. 1984 Aug;23(17):2650-5.
 - Millett F, Durham B. Design of photoactive ruthenium complexes to study interprotein electron transfer. Biochemistry. 2002 Sep 24;41(38):11315-24.
 - Qin Y, Peng Q. Ruthenium sensitizers and their applications in dye-sensitized solar cells. International Journal of Photoenergy. 2012 Jan 1;2012.
 - Nazeeruddin MK, De Angelis F, Fantacci S, Selloni A, Viscardi G, Liska P, et al. Combined experimental and DFT-TDDFT computational study of photoelectrochemical cell ruthenium sensitizers. Journal of the American Chemical Society. 2005 Dec 7;127(48):16835-47.
 - Bruneau C, Dixneuf PH, editors. Ruthenium in Catalysis. Heidelberg: Springer; 2014.
 - Wang L, Duan L, Tong L, Sun L. Visible light-driven water oxidation catalyzed by mononuclear ruthenium complexes. Journal of Catalysis. 2013 Oct 1;306:129-32.
 - Laine TM, Kärkäs MD, Liao RZ, Åkermark T, Lee BL, Karlsson EA, et al. Efficient photochemical water oxidation by a dinuclear molecular ruthenium complex. Chemical Communications. 2015;51(10):1862-5.
 - Yang Y, Liao G, Fu C. Recent advances on octahedral polypyridyl ruthenium (II) complexes as antimicrobial agents. Polymers. 2018 Jun 10;10(6):650.
 - Donnici CL, Nogueira LJ, Araujo MH, Oliveira SR, Magalhães TF, Lopes MT, et al. In vitro studies of the activity of dithiocarbamate organoruthenium complexes against clinically relevant fungal pathogens. Molecules. 2014 Apr 24;19(4):5402-20.
 - Dragutan I, Dragutan V, Démonceau A. Editorial of special issue ruthenium complex: the expanding chemistry of the ruthenium complexes. Molecules. 2015 Sep 18;20(9):17244-74.
 - Berners-Price SJ, Sadler PJ. Phosphines and metal phosphine complexes: relationship of chemistry to anticancer and other biological activity. In: Bioinorganic Chemistry 2005 Mar 3 (pp. 27-102). Berlin, Heidelberg: Springer Berlin Heidelberg.
 - Mesmaeker AK, Lecomte JP, Kelly JM. Photoreactions of metal complexes with DNA, especially those involving a primary photoelectron transfer. Electron Transfer II. 2005 May 28:25-76.
 - Mulliken RS. Electronic Population Analysis on LCAO-MO Molecular Wave Functions. I. The Journal of Chemical Physics. 1955;23:1833.
 - Mulliken RS. Electronic Population Analysis on LCAO-MO Molecular Wave Functions. II. Overlap Populations, Bond Order, and Covalent Bond Energies. The Journal of Chemical Physics.

1955;23:1841.

31. Mulliken RS. Electronic Population Analysis on LCAO-MO Molecular Wave Functions. III. Effects of Hybridization on Overlap and Gross AO Populations. The Journal of Chemical Physics. 1955;23:2338.

32. Mulliken RS. Electronic Population Analysis on LCAO-MO Molecular Wave Functions. IV. Bonding and Antibonding in LCAO and Valence-Bond Theories. The Journal of Chemical Physics. 1955;23:2343.

33. Shukla A, Mishra KK, Soni AK. sd-Hybridization, Population Analysis and MOT In Ru²⁺. I. Simple Ruthenium Dihalides. IOSR Journal of Engineering (IOSRJEN). 2019;9(12):28-37.

34. Shukla A, Mishra KK, Soni AK. sd-Hybridization, Population Analysis and MOT in Ru²⁺. II. Ruthenium mixeddihalides. IOSR Journal of Engineering (IOSRJEN). 2019;9(12):38-47.

35. Landis CR, Lipkowitz KB, Boyd DB. Reviews in Computational Chemistry. Vol. 6, VCH, 1995, Chapter 2.

36. Landis CR, Cleveland T, Firman TK. Making sense of the shapes of simple metal hydrides. Journal of the American Chemical Society. 1995 Feb;117(6):1859-60.

37. Landis CR, Firman TK, Root DM, Cleveland T. A valence bond perspective on the molecular shapes of simple metal alkyls and hydrides. Journal of the American Chemical Society. 1998 Mar 4;120(8):1842-54.

38. Tchougréeff AL, Dronskowski R. Nephelauxetic effect revisited. International Journal of Quantum Chemistry. 2009;109(11):2606-21.

39. Shimura Y. A quantitative scale of the spectrochemical series for the mixed ligand complexes of d₆ metals. Bulletin of the Chemical Society of Japan. 1988 Mar;61(3):693-8.