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RESEARCH ARTICLE

ELECTRONIC PROPERTIES OF RUTHENIUM COMPLEXES HAVING VINYL IMIDAZOLE LIGAND

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ABSTRACT

In this work, the ligands vinyl imidazole (VIm) complexes of Ruthenium(Ru) were taken and one electron redox potentials were analysed. The structures and the influence of ligand in these ruthenium complexes on the one electron transfer mechanism were investigated. Ligand charge transfer towards the Ru metal has been found prominent in these Ru-ligand complexes forming a strong coordinated bond. The one electron transfer processes of these complexes depend on the number of VIm ligands present in these complexes.

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INTRODUCTION

Tremendous interest has been shown to several ruthenium complexes because of their potential applications in anticancer drug therapy and binding with DNA /protein to probe new therapeutic agents (Zhang *et al.,* 2003; Gasser *et al.,* 2011; Ott *et al*.; Giaccone *et al.,* 2009; Jamieson *et al.,* 1999; Bergamo *et al.,* 2015; Motswainyana *et al.,* 2015). It has been shown that one of the best ways to enhance biomolecular binding is the Ru and ligand coordination and several classes of ligands such as phenanthroline, vinyl imidazole and imidazole showed formation of stable coordination bond with Ru. Over the past decade quite a large amount of studies has been reported on the relevant of electrochemical behavior of complexes with the biomolecular binding (Demeunynck *et al.,* 2003, Gielen *et al.,* 2005, Adeloye *et al.,* 2011, Vyas *et al.,* Evans *et al.,* 1973, Mitsopoulou *et al.,* 2007). It has been shown that redox behaviour of these complexes depends on the nature of the ligands, and there is a correlation between their biological property and RuII/RuIII redox. Based on the several studies of ruthenium (II) complexes containing vinyl imidazole and, it was shown that the mode of binding and biological activity of ruthenium complexes are not solely dependent on the anchoring ligands, irrespective of other factors such as molecular geometry (Juris *et al.,* 1988, Uudsemaa *et al.,* 2003). N-vinyl imidazole is known for anti-fungal, antibacterial and some other biological activities.

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In N-vinyl imidazole, imidazole ring undergoes various resonating structures to achieve a stable configuration. Therefore the compounds containing the vinyl imidazole ligands are strongly desired for improved and cost effective biological applications (Clark *et al.,* 2003; Lawrence *et al.,* 2006; Chao, 2005 Deka *et al.,* 2018). Herein, a further attempt to gain insight into the effects of ligand coordination on the one electron redox potential relevant to potential. So studies of one electron transfer mechanism of ruthenium complexes are essential to understanding the relationship between the biomolecular binding and anticancer activity (Uudsemaa *et la.,* 2003). electrochemical properties of some complexes is undertaken. Presently Ruthenium complexes have great importance in the field of medicinal chemistry particularly as anti-tumors agents. These compounds bind effectively well to DNA through various mechanisms. Different Ruthenium complexes are known for promising anticancer property due to its unique binding towards DNA. The approaches of anticancer drug design based on the mechanisms of drug binding with different bio-molecules particularly DNA. Most of the Ruthenium complexes contain important groups as well as aromatic ligands which can target to both the single and double standard nucleic acids (Baik, 2002; Hughes *et al.,* 2012; Roy, *et al.,* 2009). The ligands attached to the central metal in the complex may contribute appreciably on the selectivity of binding regions. Therefore, selection of ligands that control the stabilization of various oxidation states of the metal is very important. The redox potential of Ru metal found to be small and hence easily change to different oxidation states. Under various physiological conditions, Ruthenium may exist in

different oxidation states i.e. Ru(II), Ru(III) and Ru(IV). As a result, this property of Ru becomes very useful for targeting specific cell in biosystem and drug delivery. Activity by reduction may be another mechanism for certain Ru, predicting appropriate redox potential is important for these complexes. The energy barrier of inter-conversion among different oxidation states of Ru is relatively low and follows relatively slow ligand exchange rate in aqueous medium. Due to six coordination ability Ru can also form strong chemical bonds with biomolecules and not just to DNA. Ru causes minimal damage to healthy cells and immediately reduce to Ru(II) when targeted with cancer cells.

MATERIALS AND METHOD

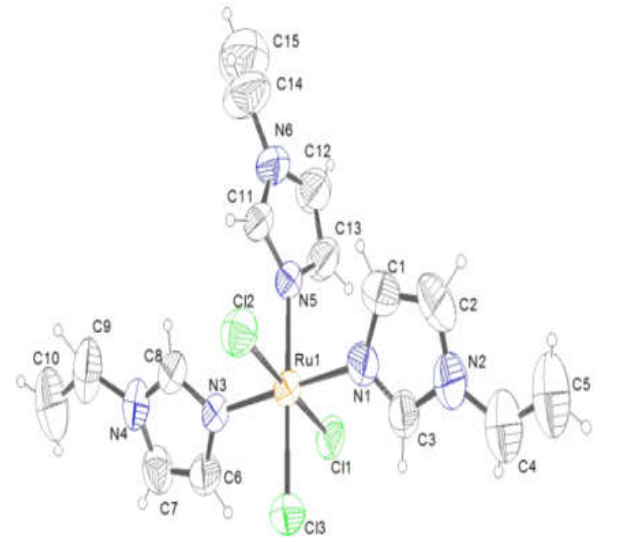
Join Molecules package was used to construct molecular models and Gaussian input (Join Molecule Kalita *et al.,* 2002). After describing the structures of the complexes with Join Molecule, complete geometry optimization and Redox energies were calculated with [Gaussian 03]. The density functional method (DFT) (B3LYP/SDD) was applied to optimize geometrical structures of complexes and ligands. The calculations of redox potentials were carried out based on the following equation. Gauss view was used for structure visualization and frontier orbital diagrams.

OX + e− → RD, i.e OX=Oxidation, RD= Reduction.

We intend to illustrate only the change in electronic energy of redox processes. Natural population analysis (NPA) was carried out to understand the charge transfer from ligand to Ru in the complex, which is the essential part of estimating the effect of ligand on the redox potentials.

RESULTS AND DISCUSSION

Theoretical concepts of the electron transfer mechanism in Ru-VIm having 3, 4 and 6 VIm ligands have not been well established. Quantum mechanical calculations are considered as useful method for calculating the electron donating or accepting ability of complexes. This may be very important in understanding the redox mechanism in electrochemical studies. The electron transfer mechanism is remarkably related to biomolecular binding which is essential for possible applications to drug discovery while selecting the biologically important ligands. The detailed information regarding the directional electron transfer mechanism is essential to monitor the selectivity of binding sites in biomolecules. So the VIm-Ru complexes are synthesized and the based on the crystal structures the electronic properties are calculated (Deka *et al.*, 2018). The crystal structures of complexes and Ligand are shown in Figures 1(a-c). The numbers of VIm ligands coordinated to Ru in these complexes are 3, 4 and 6. As we can see in the Table 1, the various oxidation and reduction potential of the complexes are not in the same range, and these values are determined without considering distinctive electron oxidation either from Ru or VIm. The structures of the Ru complexes and the ligand were completely optimized (Figures 2(a-d)) and the coordination distances of the ligand with the metal are shown in Tables 2-4. In this paper, we are going to give an overview and summarize the predicted redox potentials obtained from this computational methods. Study on the one step electron transfer mechanism is useful because most electrochemical reaction may proceed through multielectron transfer mechanism if the variation of potential of one electron transfer step is small.



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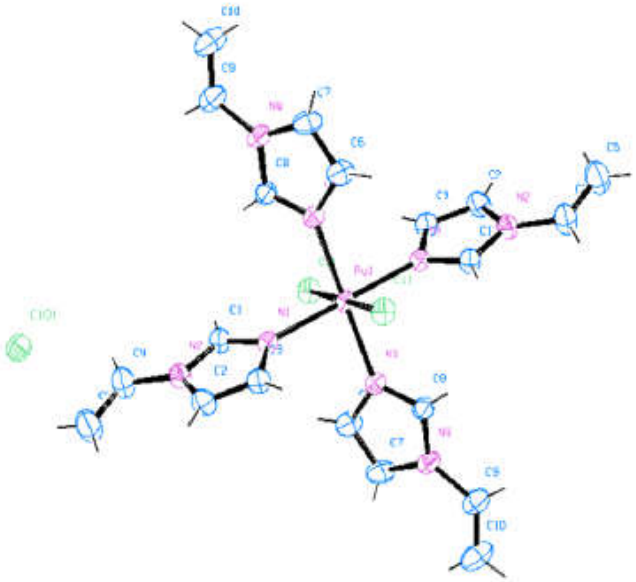

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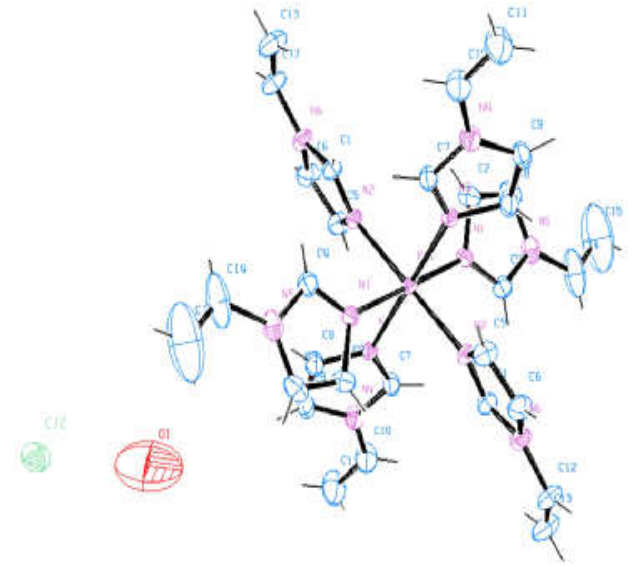

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Figure 1. Crystal structures of (a) $[Ru(VIm)_6]Cl_2$ (b) $[Ru(VIm)_4Cl_2]Cl$, (c) $[Ru(VIm)_3Cl_3]$ (Deka and Medhi, 2018).

Table 1. Redox energies of different Ru-VIm Complexes

Complexes	Status	Redox Energies E (kcalmol^{-1})
$[Ru(II)(VIm)_6]Cl_2$	Ru(II)/ Ru(III)	234.057
	Ru(II)/RD	-141.815
$[Ru(III)(Vim)_4Cl_2]Cl$	Ru(III)/Ru(IV)	398.462
	Ru(III)/Ru(II)	-314.377
$[Ru(III)(VIm)_3Cl_3]$	Ru(III)/Ru(IV)	545.925
	Ru(III)/Ru(II)	-151.227

One electron oxidation energy of VIm ligand= 197.147 kcalmol^{-1}, Reduction(RD)=-197.147 kcalmol^{-1}

Table 2. Computed NPA charges on the atoms coordinated to Ruthenium(Ru) in $[Ru(II)(VIm)_6]Cl_2$ complex along with the free ligand(VIm) and the bonds between Ru-coordinated atoms

Bond length between Ru and coordinated atom	NPA charges on atoms co-ordinated with Ru		NPA charges on atoms of free Vinyl imidazole (VIm) ligand.	
	Atom	Charges	Atom	Charges
Ru-N2 = 2.13121	N2	-0.491	N2	-0.513
Ru-N3 = 2.11331	N3	-0.459		
Ru-N10 = 2.11788	N10	-0.445		
Ru-N11 = 2.11831	N11	-0.439		
Ru-N12 = 2.11891	N12	-0.435		
Ru-N13 = 2.12159	N13	-0.465		
	Ru	0.176		

Table 3. Computed NPA charges on the atoms coordinated to Ruthenium(Ru) in $[Ru(III)(VIm)_4Cl_2]Cl$ complex along with the free ligand (VIm) and the bond length between Ru-coordinated atom

Bond length between Ru and coordinated atom(A)	NPA charges on atoms co-ordinated with Ru		NPA charges on atoms of free Vinyl imidazole(VIm) ligand.	
	Atom	Charges	Atom	Charges
Ru-N2 = 2.03708	N2	-0.227	N2	-0.513
Ru-N3 = 2.03793	N3	-0.221		
Ru-N10 = 2.03288	N10	-0.220		
Ru-N11 = 2.03708	N11	-0.220		
Ru-Cl30 = 2.44732	Cl30	0.039		
Ru-Cl31 = 2.44571	Cl31	0.118		
	Ru	0.802		

Table 4. Computed NPA charges on the atoms coordinated to Ruthenium(Ru) in $[Ru(III)(VIm)_3Cl_3]$ complex along with the free ligand (VIm) and the bond lengths between Ru-coordinated atoms

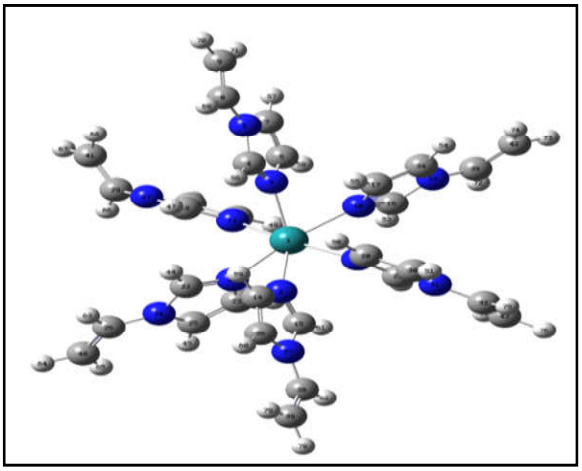
Bond length between Ru and coordinated atom(A)	NPA charges on atoms co-ordinated with Ru		NPA charges on atoms of free Vinyl imidazole(VIm) ligand.	
	Atom	Charges	Atom	Charges
Ru-N3 = 2.31616	N3	-0.482	N2	-0.513
Ru-N10 = 2.26487	N10	-0.504		
Ru-N11 = 2.10844	N11	-0.419		
Ru-Cl2 = 2.54438	Cl2	0.096		
Ru-Cl24 = 2.41951	Cl24	0.011		
Ru-Cl25 = 2.54525	Cl25	0.123		
	Ru	0.393		

Table 5. HOMO-LUMO gaps of these complexes

Complexes	$E= E_{HOMO} - E_{LUMO}$ a.u
1.$[Ru(VIm)_6]Cl_2$	-0.347
2.$[Ru(VIm)_4Cl_2]Cl$	-0.128
3.$[Ru(VIm)_3Cl_3]]$	-0.100

The outline of the analysis of one electron transfer mechanism is based on RuIII/IV and Ru III/II redox mechanisms. The VIm ligand offers the advantage of forming complexes with Ru metal through coordination bonds. This ligand unit was employed to provide electronic effect on the redox values of crystal structures of Ru complexes. The effect of VIm ligand on Ru produces variation in redox values (Table 1). However, the natural population analysis (NPA) has been carried out for these complexes and ligands, and from the charges on Ru metal and on the atoms coordinated to Ru, it is possible to understand the migration of charges from the bonding atoms of ligands to Ru (Tables 2-4). Also the bond lengths between Ru and coordinated atoms in these complexes are calculated from the optimized geometries and the values are given in Tables 2-4.

It is necessary to compute the NPA charges on the N atom of free ligand for understanding the directional electron transfer towards Ru during complexation. Moreover, the values of one electron transfer must be given enormous importance to understand electron lability in redox reaction. From these values, it is possible to understand the capability of electron donation or transfer towards certain biomolecules during binding. Furthermore the values of oxidation and reduction potentials of $(Ru(VIm)_6]$ Cl_2, $(Ru(VIm)_4Cl_2]Cl$ and $(Ru(VIm)_3Cl_3]$ are significantly different (Table 1). The oxidation of $(Ru(VIm)_6]$ Cl_2 from Ru(III) to Ru(IV) may be less favourable since the oxidation energies are comparatively larger than reduction energies and one electron oxidation energy of VIm ligand.



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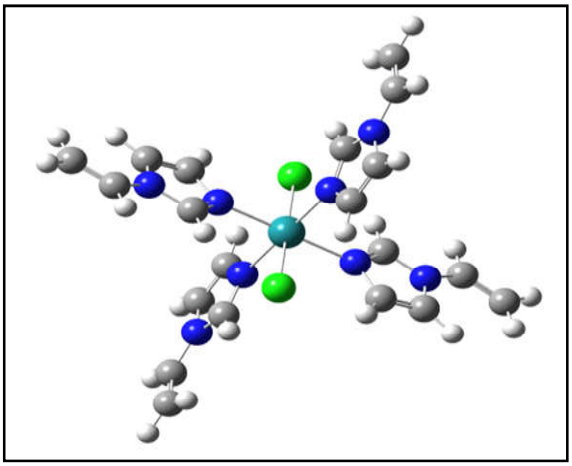

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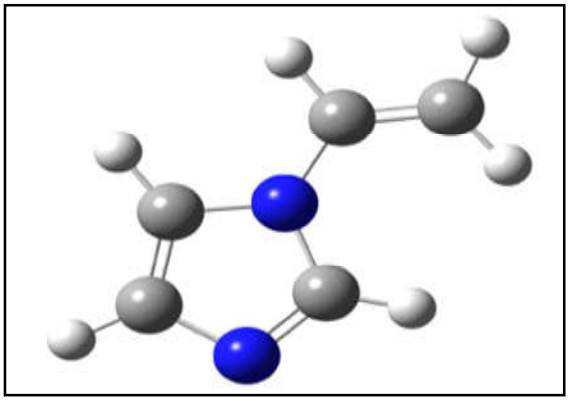

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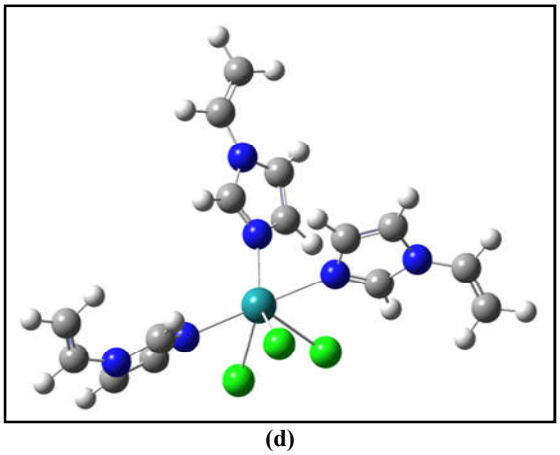


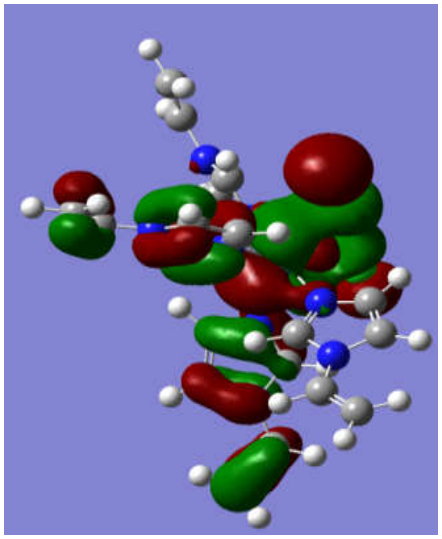
(d)

Figure 2. Structures of (a) $[Ru(VIm)_6]$, (b) $[Ru(VIm)_4Cl_2]$, (c) $[Ru(VIm)_3Cl_3]$, (d) Vinyl Imidazole(VIm)

We have computed the reduction energy value of $(Ru(II)(VIm)_6]\ Cl_2$ hypothetically and the value is found less than ligand reduction energy. Similary, the oxidation energies Ru(III) to Ru(IV) of $(Ru(VIm)_4Cl_2]Cl$ and $(Ru(VIm)_3Cl_3]$ are larger than that of $[Ru(VIm)_6]\ Cl_2$. Moreover for the reduction energies have increased significantly. The electron transfer potentials obtained from experimental measurements are solvent dependant and the absolute values of electron transfer potential cannot be measured. So the absolute values obtained from theoretical study are necessary for comparison of electron lability among these complexes. So the influence of VIm on the redox energies should be prominent. The NPA charge on Ru in $(Ru(VIm)_6]Cl_2$ less than that of $(Ru(VIm)_4Cl_2]Cl$ and $(Ru(VIm)_3Cl_3]$ and hence the redox energies of $(Ru(VIm)_6]Cl$ are comparatively small. The lability of electron of $(Ru(VIm)_6]\ Cl_2$ is better than that of $(Ru(VIm)_4Cl_2]$ and$[Ru(VIm)_3Cl_3]$ this may be related to the efficiency of binding of these complexes with biomolecules. However, the mechanism of complex binding for $(Ru(VIm)_3Cl_3]$ and $(Ru(VIm)_4Cl_2]Cl$ may be due to the dissociation of Cl and further coordination of Ru with the binding site. Such mechanism may not take place in $(Ru(VIm)_6]\ Cl_2$.

The charge density on N1(Ru bonded atom) of VIm ligand is significantly decreased in these complexes compared to that of free VIm ligand. Hence, the donating ability of ligand and the redox potential may also be related. It is possible to choose the biologically active ligand which is compatible to biological potential system for enhancing drug efficacy. Tables 2 and 4 show the variation of Ru-N lengths of all these complexes. Comparatively shorter bond lengths indicate the tightness of Ru-N bonds. The variations of oxidation and reduction energies of $Ru(VIm)_4Cl_2]Cl$ are not very large compared to other complexes. The charges on bonding nitrogen atoms of VIm ligands in the complex $(Ru(VIm)_6]\ Cl_2$, $Ru(VIm)_4Cl_2]Cl$ and $(Ru(VIm)_3Cl_3]$ are examined and the computed values are given in Tables 2-4. The NPA values of coordinating N atom and Ru of these complexes can be compared with that of free ligand, and migration of charges from N aromatic ring towards ligand has been found.

The extent of charge transfer from N aromatic ring is clearly indicated from the decrease of NPA charge of ligand N atoms after forming coordination bonds with Ru. There are three VIm ligand in $(Ru(VIm)_3Cl_3)$. All the coordination bonds lengths are approximately 2.0-2. 3Å (Tables 2-4). Another prominent feature in $(Ru(VIm)_6]Cl_2$ is that the coordination bond lengths between Ru and N of VIm ligands are equal and maintains symmetrical arrangement of ligands. In $(Ru(VIm)_3Cl_3]$ and $(Ru(VIm)_4Cl_2]Cl$ complexes small differences in coordination distances are observed. We observed significant variation of NPA charges on N atom of VIm after coordination with Ru. To have an insight into the extent of charge transfer from VIm towards Ru in all these three complexes, we can compare the NPA charges on Ru from Tables 2-4. From the optimized structures shown in Figures 2a-c as well as the coordination bond lengths displayed in Tables 2-4, the orientation of VIm coordination bond lengths can be compared. The coordination bond length increases of the order $(Ru(VIm)_4Cl_2]$ $Cl>[Ru(VIm)_6]Cl_2>[Ru(VIm)_3Cl_3)$. The computed bond parameters are indicative of bonding ability of VIm with Ru and one can indirectly guess the stability of these complexes. The optimized structures and configuration of VIm ligand can be examined which are based on the local geometrical features of the crystal structures of complexes (Figures 1a-c).



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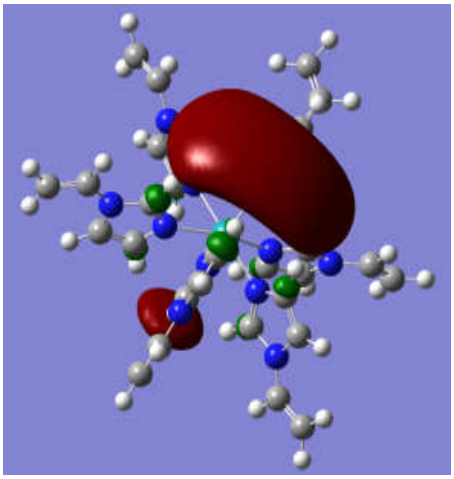

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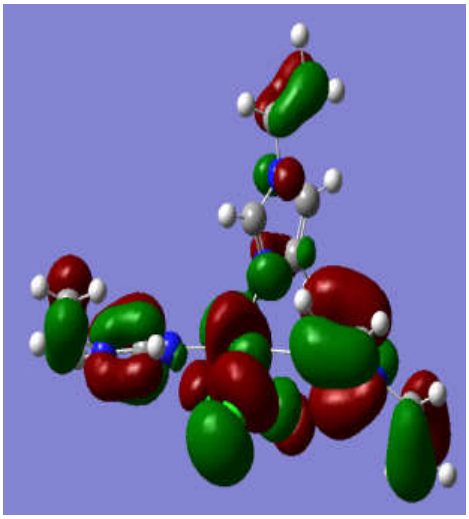

(c)

Figure 3. Frontier orbital diagrams of (a) $[Ru(VIm)_6]Cl_2$, (b) $[Ru(VIm)_4Cl_2]Cl$, (c) $[Ru(VIm)_3Cl_3]$

The values of Ru–N bond lengths in these complexes depend on the number of VIm bonded to Ru where much comparatively longer bond lengths are found in $(Ru(VIm)_3Cl_3]$ and $Ru(VIm)_6]Cl_2$. This may be due to either steric effect or additional stacking interactions among VIm ligands. The theoretical geometrical parameters are quite close to the experimental values (Deka J *et al.,* 2018). Since the crucial electronic effect resulting the change in redox potential of these complexes arise from the highest occupied molecular orbitals (HOMO) to the lowest unoccupied molecular orbitals (LUMO) (Tables 1 and 5). In such situation it is important to examine the HOMO localized and the LUMO in these complexes. Figure 3a-c show the position of HOMO in these complexes and the difference of HOMO-LUMO energies in given in Table 5. The position HOMO orbital density is located around the Ru metal in$[Ru(VIm)_6]Cl_2$, but well located towards the VIm ligands in $(Ru(VIm)_4Cl_2]Cl$ and $(Ru(VIm)_3Cl_3]$. The HOMO-LUMO gap is decreasing order of the complexes $(Ru(VIm)_6]$ Cl_2 $<[Ru(VIm)_4Cl_2]Cl<[Ru(VIm)_3Cl_3)$. These results may indicate importance in differentiating the electron transfer features of these complexes, which may take place either through Ru coordination or ligand binding.

Conclusion

In this work, the molecular structures and redox energies of some Ru-VIm complexes are studied. The density functional theory (B3LYP/SDD) methodology is useful for understanding the crystal structures and frontier orbitals of these complexes. The molecular geometries and Ru-N (VIm heterocyclic ring) bond distances depend on the number of VIm present in these complexes. The redox energies of these complexes vary significantly and the oxidation energies are much larger than one electron VIm ligand oxidation. The HOMO orbital density is located over around the ligand molecules in $(Ru(VIm)_4Cl_2]Cl$ and $(Ru(VIm)_3Cl_3]$ but spreads around Ru in $(Ru(VIm)_6]Cl_2$. The redox energies may be useful for analyzing one electron transfer mechanism of these complexes.

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