Computational Study of Rutehnium(Ii)-Benzimidazole Complex

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ABSTRACT

The computational study of $[Ru(H_2pbbzim)_2]^{2+}$(H_2pbbzim = 2,6bis(benzimidazole-2-yl)pyridine) complex having tridentate ligands has been investigated using Gaussian 09 software. The DFT calculation of the complex is carried out by the B3LYP method in the LANL2DZ basis set. Thebond lengths and the bond angles of the complex can be determined from the optimized structure. Quantum chemical parameters like E_{HOMO}, E_{LUMO}, HOMO-LUMO energy gap, chemical potential, electronegativity, chemical hardness, ionization energy, electron affinity, Softness and electrophilicity index of the $[Ru(H_2pbbzim)_2]^{2+}$complex is calculated. The energy gap of $[Ru(H_2pbbzim)_2]^{2+}$complex obtained from the theoretical calculation is0.7319 eV. The theoretical values predict that $[Ru(H_2pbbzim)_2]^{2+}$complex is appropriate for optical sensing studies. Thus, the computation study may shed some light on the future applications of the complex.

Keywords: Computational study, $[Ru(H_2pbbzim)_2]^{2+}$complex, DFT calculation, Quantum chemical parameters

Introduction

Transition metal-based materials are much more advantageous over pure organic frameworks, as they can offer better tunability of the structural, optical, electrochemical and electronic properties [1]. Among the various transition metals, coordination complexes based on Ru(II) metal are considered as potential building blocks for the design of suitable functional materials, as they possess outstanding photophysical and optoelectronic properties which primarily evolve from their metal to ligand charge transfer (MLCT) excited states [2,3].

Ruthenium complexes are widely used and studied in different chemical fields. They attract the attention of researchers due to their high stability and the easy modification of their

properties by employing carefully controlled synthetic methods. Complexes bearing π-conjugated ligands or systems that enable electronic delocalization have shown specific

properties in non-linear optics, magnetism, molecular sensing and liquid crystals. However, the most employed are ruthenium complexes with heterocyclic N-donor ligands due to their interesting spectroscopic, photophysical and electrochemical properties. These may be taken into advantage for their application as photosensitizers for photoactive conversion of solar energy, molecular electronic devices and photoactive DNA cleavage agents for therapeutic purposes [4].

Benzimidazole derivatives have attracted strong research interest due to their potential applications in coordination chemistry, asymmetric catalysis, chemo-therapeutics and supramolecular chemistry. The Ru(II) complexes of benzimidazole derivatives are practically non-luminescent at room temperature and their excited state lifetime are also very short. Therefore, much effort has been devoted to design and synthesise tridentate polypyridine ligands that can produce Ru(II) complexes with enhanced emission quantum yields and excited-state lifetimes. Most of the approaches aim to increase the energy gap between the radiative ^{3}MLCT and quenching ^{3}MC (metal centred) states.

Design of molecular systems capable of responding to a specific set of ionic inputs is important for the constructions of effective sensors and molecular logic devices. Density Functional Theory (DFT) and Time-Dependent Density Functional Theory (TD-DFT) have become a popular tool for computing the optical and spectral properties of the complexes. In order to understand the physical and quantum chemical parameters of Ru(II) complexes, the present investigation focuses on the computational study of $[Ru(H_2pbbzim)_2]^{2+}$complex in LANL2DZ basis set by B3LYP method using Gaussian 09 software.

Methodology

The $[Ru(H_2pbbzim)_2]^{2+}$complex has been drawn in AVOGADRO software and MOPAC software was used for the pre-optimisation of the complex using semi empirical method. The program Gaussian 09 was employed to perform DFT and TD- DFT calculations on $[Ru(H_2pbbzim)_2]^{2+}$complex. HOMO-LUMO energy level calculation and geometry optimization have been carried out using LANL2DZ Basis set and optimized molecular structure was visualized by Gauss view (6.0.16) program.

The physical and quantum chemical parameters of $[Ru(H_2pbbzim)_2]^{2+}$complex were analysed by DFT studies. The quantum chemical descriptors were defined as the partial derivatives of the total electronic energy (E) with respect to the number of electrons (N) at a

fixed external potential. Quantum chemical parameters like E_{HOMO}, E_{LUMO}, HOMO-LUMO energy gap, chemical potential (μ), electronegativity (χ), chemical hardness (η) ionization energy (I), electron affinity (A), Softness (σ) and electrophilicity index (ω) of the $[Ru(H_2pbbzim)_2]^{2+}$complex was calculated from the following equations[5].

$$\mu = -\chi = \left(\frac{\partial E}{\partial N}\right)_{v(r)} \quad \text{---------- (1)}$$

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)} = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{v(r)} \quad \text{---------- (2)}$$

$$\chi = -\mu = \left(\frac{I + A}{2}\right) \quad \text{---------- (3)}$$

$$\chi = -\mu = \frac{-E_{HOMO} - E_{LUMO}}{2} \quad \text{---------- (4)}$$

$$\eta = \frac{E_{HOMO} - E_{LUMO}}{2} \quad \text{---------- (5)}$$

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta} \quad \text{---------- (6)}$$

$$\varepsilon = 1/\omega \quad \text{---------- (7)}$$

$$\sigma = 1/\eta \quad \text{---------- (8)}$$

Results and Discussion

Ground-state electronic structure calculations of $[Ru(H_2pbbzim)_2]^{2+}$complexunder investigation have been done using the DFT method. The optimized structure gives the basic information such as empirical formula, molecular weight, point group and planar/ non-planar nature of $[Ru(H_2pbbzim)_2]^{2+}$complex. The calculated empirical formula, molecular weight and point group of $[Ru(H_2pbbzim)_2]^{2+}$ complex is$C_{38}H_{26}N_{10}Ru$, 723.7604 and C_1 point group respectively.The geometry optimization of $[Ru(H_2pbbzim)_2]^{2+}$ complex yields non-planar structure (**Fig. 1**).

The geometrical parameters of $[Ru(H_2pbbzim)_2]^{2+}$ complex can be determined from the optimized structure. The bond length of C=C in $[Ru(H_2pbbzim)2]^{2+}$ complex is in between 1.4017 - 1.4187 A^o(**Table 1**). The bond lengths of C_3-C_{17}, C_5-C_7, C_9-C_{14}, C_{19}-C_{24}, C_{39}-C_{53}, C_{41}-C_{43}, C_{45}-C_{50} and C_{55}-C_{60} are slightly higher (~1.43A^o), this is due to the presence of electronegative N atom. Ru-N bond lengths are observed in this complex within the range 2.020 - 2.102A^o. In $[Ru(H_2pbbzim)_2]^{2+}$ complex the bivalent metal is coordinated by the

tridentate ligand and has a distorted octahedral geometry having a meridional N3N3 chromophore. The chelate bite angles span the range between 77.87° and 77.94°. The inter ligand trans angle of N_4-Ru-N_{40} is 179.95° and is very close to linearity, the intra ligand trans angle N_8-Ru-N_{25} and N_{44}-Ru-N_{61} are 157.82° and deviates significantly from linearity.

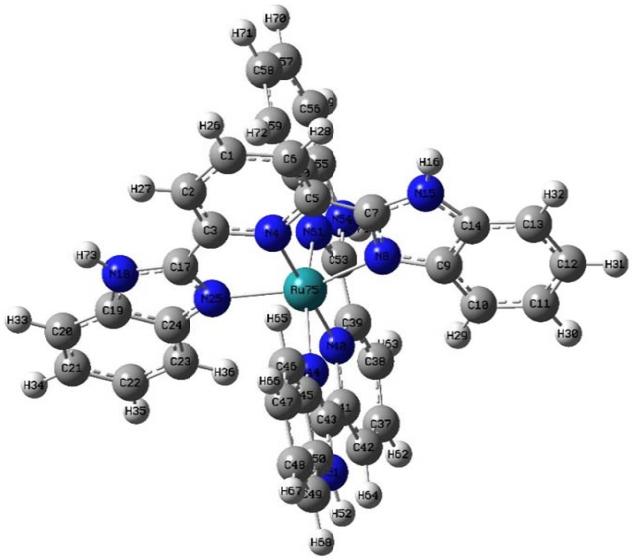


Fig. 1 Optimized geometry of $[Ru(H_2pbbzim)_2]^{2+}$ complex obtained at B3LYP/LANL2DZ

Quantum chemical parameters E_{HOMO}, E_{LUMO}, HOMO-LUMO energy gap, chemical potential (μ), electronegativity (χ) and chemical hardness (η) ionization energy (I), electron affinity (A), Softness (σ) and electrophilicity index (ω) of $[Ru(H_2pbbzim)_2]^{2+}$ complex in the gas phase has been calculated and presented in **Table 2**

Table 1 Bond length of $[Ru(H_2pbbzim)_2]^{2+}$ complex obtained by DFT calculation

Atoms	Bond Length (A°)	Atoms	Bond Length (A°)
C_1-C_2	1.4175	C_{37}-C_{38}	1.4175
C_1-C_6	1.4187	C_{37}-C_{42}	1.4187
C_1-H_{26}	1.0858	C_{37}-H_{62}	1.0858
C_2-C_3	1.4024	C_{38}-C_{39}	1.4024
C_2-H_{27}	1.0878	C_{38}-H_{63}	1.0878
C_3-N_4	1.3999	C_{39}-N_{40}	1.3999

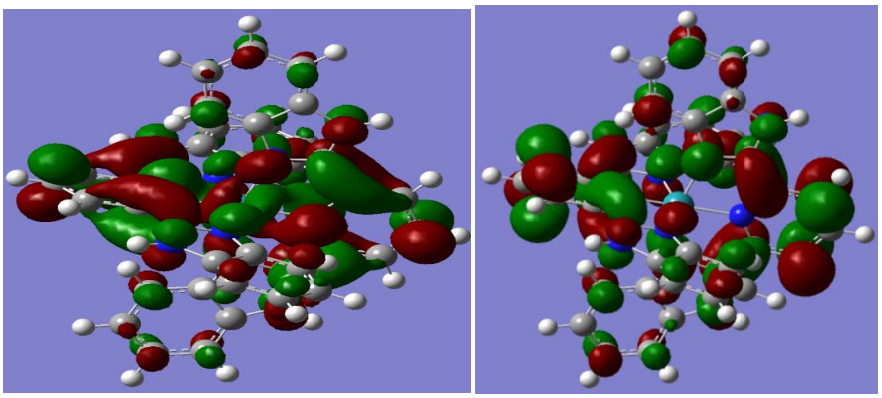
C_3-C_{17}	1.4344	C_{39}-C_{53}	1.4344
N_4-C_5	1.3980	N_{40}-C_{41}	1.3980
N_4-Ru_{75}	2.0200	N_{40}-Ru_{75}	2.0200
C_5-C_6	1.4017	C_{41}-C_{42}	1.4017
C_5-C_7	1.4359	C_{41}-C_{43}	1.4359
C_6-H_{28}	1.0877	C_{42}-H_{64}	1.0877
C_7-N_8	1.3732	C_{43}-N_{44}	1.3731
C_7-N_{15}	1.3971	C_{43}-N_{51}	1.3971
N_8-C_9	1.3990	N_{44}-C_{45}	1.3990
N_8-Ru_{75}	2.1015	N_{44}-Ru_{75}	2.1016
C_9-C_{10}	1.4070	C_{45}-C_{46}	1.4070
C_9-C_{14}	1.4309	C_{45}-C_{50}	1.4308
C_{10}-C_{11}	1.4060	C_{46}-C_{47}	1.4060
C_{10}-H_{29}	1.0851	C_{46}-H_{65}	1.0851
C_{11}-C_{12}	1.4181	C_{47}-C_{48}	1.4181
C_{11}-H_{30}	1.0873	C_{47}-H_{66}	1.0873
C_{12}-C_{13}	1.4098	C_{48}-C_{49}	1.4098
C_{12}-H_{31}	1.0874	C_{48}-H_{67}	1.0874
C_{13}-C_{14}	1.4027	C_{49}-C_{50}	1.4027
C_{13}-H_{32}	1.0869	C_{49}-H_{68}	1.0869
C_{14}-N_{15}	1.4014	C_{50}-N_{51}	1.4014
N_{15}-H_{16}	1.0089	N_{51}-H_{52}	1.0089
C_{17}-N_{18}	1.3977	C_{53}-N_{54}	1.3977
C_{17}-N_{25}	1.3742	C_{53}-N_{61}	1.3742
N_{18}-C_{19}	1.4015	N_{54}-C_{55}	1.4015
N_{18}-H_{73}	1.0089	N_{54}-H_{74}	1.0089

C_{19}-C_{20}	1.4025	C_{55}-C_{56}	1.4025
C_{19}-C_{24}	1.4310	C_{55}-C_{60}	1.4310
C_{20}-C_{21}	1.4101	C_{56}-C_{57}	1.4101
C_{20}-H_{33}	1.0870	C_{56}-H_{69}	1.0870
C_{21}-C_{22}	1.4179	C_{57}-C_{58}	1.4179
C_{21}-H_{34}	1.0874	C_{57}-H_{70}	1.0874
C_{22}-C_{23}	1.4063	C_{58}-C_{59}	1.4063
C_{22}-H_{35}	1.0873	C_{58}-H_{71}	1.0873
C_{23}-C_{24}	1.4071	C_{59}-C_{60}	1.4071
C_{23}-H_{36}	1.0851	C_{59}-H_{72}	1.0851
C_{24}-N_{25}	1.3986	C_{60}-N_{61}	1.3986
N_{25}-Ru_{75}	2.1003	N_{61}-Ru_{75}	2.1002

Table 2 Quantum chemical parameters of $[Ru(H_2pbbzim)_2]^{2+}$ complex

Parameters	**$[Ru(H_2pbbzim)_2]^{2+}$ (eV)**
E_{HOMO}	-2.272
E_{LUMO}	-1.5401
Energy gap	0.7319
Ionization energy	2.272
Electron affinity	1.5401
Electronegativity	1.90605
Chemical potential	-1.90605
Chemical hardness	0.36595
Softness	1.366307
Electrophilicity index	4.963829

The energy level diagram of $[Ru(H_2pbbzim)_2]^{2+}$ complex is shown in **Fig. 2**. The electronic absorption is mainly described by one electron excitation from HOMO to LUMO. Both HOMO and LUMO are the main orbitals that take part in chemical stability. These orbitals play an important role in the electronic properties and determine the way the molecule interacts with other species [6,7]. The energy of HOMO and LUMO in $[Ru(H_2pbbzim)_2]^{2+}$ complexis directly related to ionization potential and electron affinity.



LUMO HOMO

Fig. 2 Energy level diagram for $[Ru(H_2pbbzim)_2]^{2+}$ complex

The frontier orbital gap between HOMO and LUMO, represents the stability of structure and helps to determine the kinetic stability and the chemical reactivity of the molecule. Chemical hardness is also associated with the stability and reactivity of a chemical system. The energy gap value of $[Ru(H_2pbbzim)_2]^{2+}$complex is 0.7319 eV which reflects the chemical activity of the molecule. The Frontier Molecular orbitals of $[Ru(H_2pbbzim)_2]^{2+}$ complex are shown in **Fig. 3.** This small energy gap confirms that the $[Ru(H_2pbbzim)_2]^{2+}$ complex is highly reactive and polarizable. Thus, the theoretical values predict that $[Ru(H_2pbbzim)_2]^{2+}$complex is appropriate for optical sensing studies.

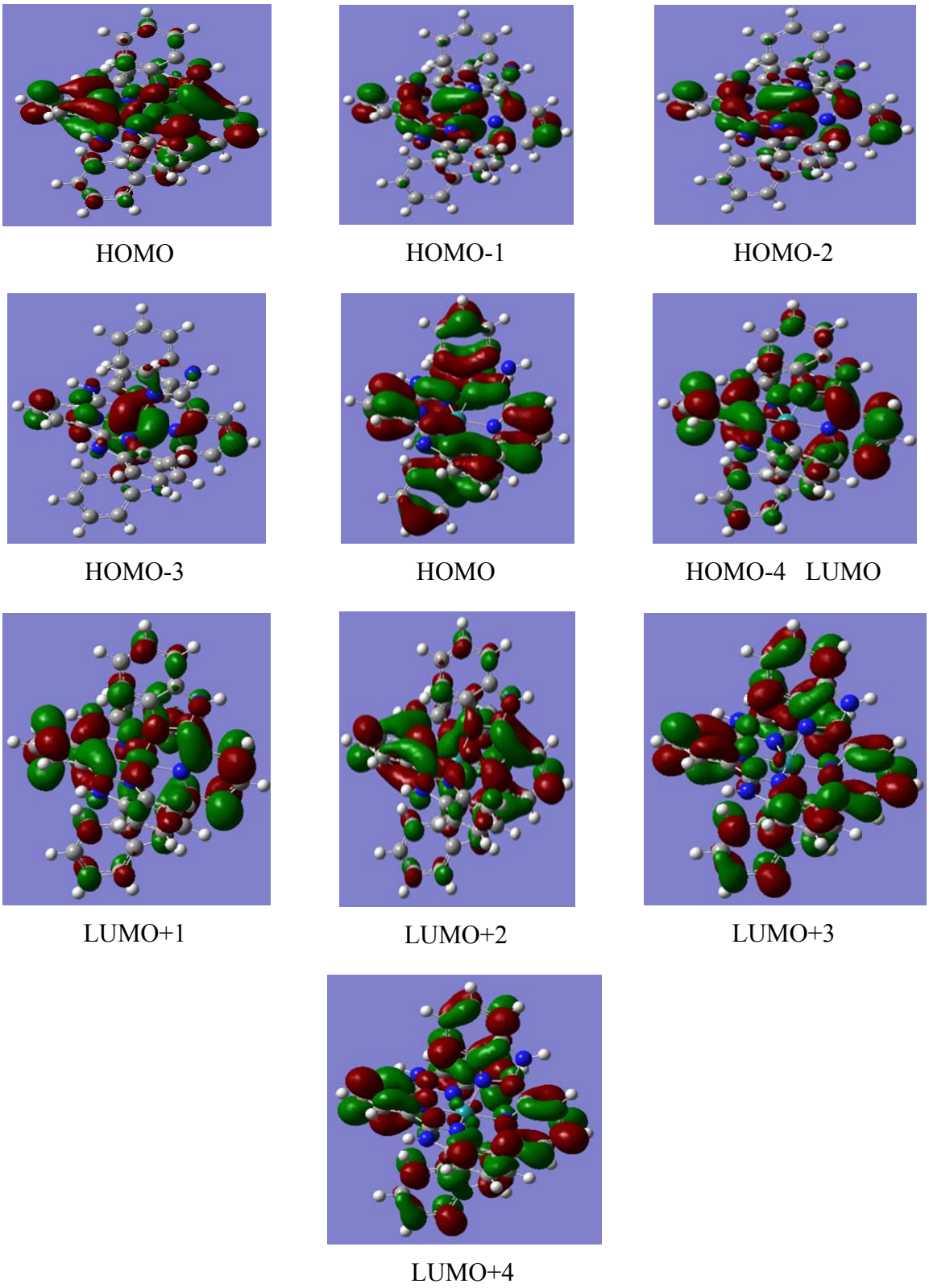


Fig. 3 Frontier molecular orbitals of $[Ru(H_2pbbzim)_2]^{2+}$ complex

Conclusion

The Ru(II) complex having tridentate H_2pbbzim ligands has been designed and the theoretical calculations have been carried out using the LANL2DZ basis set. The physico-chemical parameters of the complex have been calculated using the DFT method. The energy gap of$[Ru(H_2pbbzim)_2]^{2+}$ complexis found to be 0.7319 eV. This small HOMO-LUMO energy gap of $[Ru(H_2pbbzim)_2]^{2+}$ complexconfirms the chemical reactivity and the polarizability of the complex. The theoretical energy gap value indicates that the metal complex is suitable for further studies. Quantum chemical parameters also predict that this complex is appropriate for optical sensing studies. Thus, the computation study may shed some light on future applications of $[Ru(H_2pbbzim)_2]^{2+}$ complex.

References

1. Bar M., Deb S., Paul A., Baitalik S. Stimuli-responsive luminescent bis-tridentate Ru(II) complexes toward the design of functional materials. Inorg. Chem. 2018; 57: 12010-12024.
2. Balzani V., Juris A., Venturi M., Campagna S., Serroni S. Luminescent and redox-active polynuclear transition metal complexes. Chem. Rev. 1996; 96: 759-834.
3. Sauvage J.P., Collin J.P.J., Chambron C., Guillerez S., Coudret C., Balzani V., Barigelletti F., Cola D.L., Flamigni, L. Ruthenium(II) and Osmium(II) bis(terpyridine) complexes in covalently-linked multicomponent systems: Synthesis, electrochemical behaviour, absorption spectra, and photochemical and photophysical properties. Chem. Rev. 1994; 94: 993-1019.
4. Garino C., Terenzi A., Barone S., Salassa G.L. Teaching inorganic photophysics and photochemistry with three ruthenium(II) polypyridyl complexes: A computer-based exercise. J. Chem. Educ. 2016; 93: 292-298.
5. Muthukkumar M., Kamal C., Venkatesh G., Kaya C., Kaya S., Enoch I.V.M.V., Vennila P., Rajave R. Structural, spectral, DFT and biological studies on macrocyclic mononuclear ruthenium (II) complexes. J. Molecular Structure. 2017; 1147: 502-514.
6. Kamalesu S., Swarnalatha K., Subramanian R., Muralidharan K., Gomathi S., Polypyridyl-hydrazone based ruthenium(II) complexes: Spectral and computational analysis. Inorganica Chimica Acta, 2017; 461: 35-44.
7. Morales Y.R. HOMO-LUMO gap as an index of molecular size adn structure for ploycyclic aromatic hydrocarbons (PAHs) and asphaltenes: A theoretical study. J. Phys. Chem. A. 2002; 106: 11283-11308.