

Structure, characterization and molecular structure of Ru(III) complexes

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Abstract— A series of azopyrazolones (HL_n) were synthesized from the coupling of 3-(2-hydroxyphenyl)-5-phenyl-4,5-dihydro-1H-pyrazole with aniline and its *p*-derivatives. These ligands and their Ru(III) complexes (1-3) of the type $[Ru(L_n)(Cl)_2(H_2O)_2]$ were prepared and characterized by elemental analysis, IR, and UV-Visible spectra as well as magnetic and thermal measurements. The molar conductance measurements proved that all the complexes are non-electrolytes. IR spectra show that the ligands (HL_n) acts as a monobasic bidentate ligand by coordinating via the nitrogen atom of the pyrazole ring ($-HN=N=$) and oxygen atom of the deprotonated $-OH$ group moiety, thereby forming a six-membered chelating ring and concomitant formation of an intramolecular hydrogen bond. Analytical data revealed that all the complexes exhibited 1:1 metal-ligand ratio. The molecular and electronic structures of the investigated Ru(III) complexes were also studied using quantum chemical calculations. The optimized bond lengths, bond angles and calculated the quantum chemical parameters for the complexes were investigated.

Index Terms— Ru(III) complexes; Azopyrazolones; Molecular structure.

1 INTRODUCTION

Azo compounds are very important molecules and have attracted much attention in both academic and applied research [1]. Azo compounds consists of at least a conjugated chromophore azo ($-N=N-$) group in association with one or more aromatic or heterocyclic system. Commercially, these colorants are the largest and most versatile class of organic dyestuffs [2]. The widest usage of the azo dyes is due to the number of the variations in the chemical structure and the methods of application which are generally not complex. Aryl azo pyrazolones generally have a high molar extinction coefficient, medium to high light and wash fastness properties [3]. In recent years, azo dyes have attracted wide interest and found many uses in various fields such as dyeing of textile fibers, coloring of different materials, biological-medical studies, organic synthesis and advanced applications including optical storage capacity, optical switching, holography and non-linear optical properties [4].

Amongst the transition metals, ruthenium displays an especially diverse coordination and organometallic chemistry, including a vast array of stable complexes with every conceivable type of ligand [5]. The chemistry of ruthenium complexes is of significant importance [6], because of the fascinating rela-

tivities exhibited by the resultant complexes and the nature of the ligands that dictates the property of those complexes. Ruthenium compounds have been the subject of great interest and impressive development in last decades for many reasons, especially due to their catalytic [7] and anticancer activities [8]. Ruthenium generally demonstrates affinity toward N-donor molecules such as proteins and DNA. The mechanism of the action of antitumor-active ruthenium compounds is not entirely known. Closely, it is thought that the complexes containing chlorides, or other easily leaving group, can hydrolyze in vivo, allowing the covalent binding of the nucleobases from DNA to ruthenium [9]. Many Ru(II) and Ru(III) compounds with numerous different ligands are reasonably synthesized and investigated for the purpose of possible application in medicine and catalysis.

On the other hand, significant interactions of anticancer ruthenium(III) compounds with potential protein targets were recently described [10]. Moreover, detailed knowledge of the interactions of antitumor ruthenium(III) complexes with plasma proteins is of interest because binding to proteins might result in drastic modification, or even loss, of the biological properties of the starting compounds. Alterna-

tively, a protein-bound ruthenium species might still represent an active species, provided that some amount of ruthenium is transported through the biological fluids and eventually released at the cellular level [11].

Herein, we report the synthesis and characterization of Ru(III) complexes by different spectroscopic techniques. IR spectra show that the ligands (**HL_n**) acts as a monobasic bidentate ligand by coordinating via the nitrogen atom of the pyrazole ring (-HN-N=) and oxygen atom of the phenolic OH group with the displacement of the hydrogen atom from the later group. The optimized bond lengths, bond angles and calculated the quantum chemical parameters for the complexes were investigated.

2. Materials and methods

2.1. Materials and apparatus

Hydrated ruthenium(III) chloride (98%) were purchased from Sigma-Aldrich. All reagents and solvents were purchased from Aldrich, Fluka and Merck and were used without any further purification.

Microanalytical data (C, H and N) were collected on Automatic Analyzer CHNS Vario ELIII, Germany. Spectroscopic data were obtained using the following instruments: FT-IR spectra (KBr discs, 4000-400 cm⁻¹) by Jasco FTIR-4100 spectrophotometer; UV-Visible spectra by Perkin-Elmer AA800 spectrophotometer Model AAS. Thermal analysis of Ru(III) complexes were carried out using a Shimadzu thermogravimetric analyzer under a nitrogen atmosphere with heating rate of 10 °C/min over a temperature range from room temperature up to 800 °C. Magnetic susceptibility measurements were determined at room temperature on a Johnson Matthey magnetic susceptibility balance using Hg[Co(SCN)₄] as calibrant. Effective magnetic moments were calculated based on the equation: $\mu_{\text{eff}} = 2.84 (X_M^{\text{corr}} T)^{1/2}$. Conductivity measurements of the complexes at 25 ± 1 °C were determined in DMF (10⁻³ M) using conductivity/TDS meter model Lutron YK-22CT. The molecular structures of the investigated compounds were optimized by HF method with 3-21G basis set. The molecules were built with the Perkin Elmer ChemBio Draw and optimized using

Perkin Elmer ChemBio3D software [12].

2.2.. Preparation of 3-(2-hydroxy-5-(4-arylozo))-5-phenyl-4,5-dihydro-1H-pyrazole (**HL_n**)

The azo compounds of 3-(2-hydroxy-5-(4-arylozo))-5-phenyl-4,5-dihydro-1H-pyrazole (**HL_n**) were prepared previously [13] by coupling of diazonium salt of aniline or its p-derivatives (0.01 mol) with 3-(2-hydroxyphenyl)-5-phenyl-4,5-dihydro-1H-pyrazole (0.01 mol) [14]. The solid azo dyes were collected by filtration, washed several times with water, dried in a vacuum desiccator over anhydrous CaCl₂. The formed azo compounds were recrystallized from methanol to give colored crystals of compounds (**HL_n**).

For **HL₁**: Yield, 70%. Analysis: Found: C 73.45%, H 5.28%, N 16.45%. Calculated for C₂₁H₁₈N₄O: C 73.66%, H 5.30%, N 16.36%. For **HL₂**: Yield, 65%. Analysis: Found: C 70.80%, H 5.42%, N 15.10%. Calculated for C₂₂H₂₀ N₄O₂: C 70.95%, H 5.41%, N 15.04%. For **HL₃**: Yield, 65%. Analysis: Found: C 66.80%, H 4.55%, N 14.60%. Calculated for C₂₁H₁₇ClN₄O: C 66.93%, H 4.54%, N 14.87%.

HL₁ = (E)-2-(5-phenyl-4,5-dihydro-1H-pyrazol-3-yl)-4-(phenyldiazenyl)phenol

HL₂ = (E)-4-((4-methoxyphenyl)diazenyl)-2-(5-phenyl-4,5-dihydro-1H-pyrazol-3-yl)phenol

HL₃ = (E)-4-((4-chlorophenyl)diazenyl)-2-(5-phenyl-4,5-dihydro-1H-pyrazol-3-yl)phenol

2.3. Synthesis of Ru(III) complexes

All Ru(III) complexes were synthesized according to the general procedure [9]: a stoichiometric amount of the desired ligand (0.01 mol) in methanol (20 cm³) was added dropwise to a hot methanol solution (20 cm³) of RuCl₃.3H₂O (0.01 mol) with stirring and the reaction mixture was refluxed for 3 h. The solution was concentrated to half of its original volume by evaporation and allowed to cool at room temperature. During this, a microcrystalline solid was separated, which was isolated by filtration, washed with hot methanol, ether and dried in a vacuum desiccator over anhydrous CaCl₂.



3. Results and discussion

The results of physical properties of the prepared ligands and their Ru(III) complexes along with their elemental analysis are collected in Table 1. The analytical data of Ru(III) complexes indicated that the complexes have 1:1 (metal:ligand) stoichiometry. The Ru(III) complexes are stable in air and soluble in most common organic solvents. The molar conductance values for the ruthenium(III) complexes (10^{-3} M) are measured in DMF and these values are ($8-10 \Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$) range indicating the non-electrolytic nature of the complexes. The room temperature magnetic moment values (μ_{eff}) per ruthenium ion for the complexes were in 1.79-2.53 BM range. These values lies within the range of the spin only value of one unpaired electron [15], which corresponds to Ru^{3+} state (low spin).

Table 1. Physical properties and elemental analyses data of Ru(III) complexes (1-3).

| Comp | Structure | Molecular Formula | Mol. Weight | M.P. (°C) | Yield (%) | Color | Calculated (Found) % | | |
|------|---|---|-------------|-----------|-----------|-------|----------------------|--------|--------|
| | | | | | | | C | H | N |
| 1 | [Ru(L ₁)(Cl) ₂ (H ₂ O) ₂] | C ₂₁ H ₂₃ RuN ₄ O ₅ Cl ₂ | 549.41 | >300 | 80 | Green | 45.90 | 3.85 | 10.19 |
| | | | | | | | (44.76) | (3.15) | (7.44) |
| 2 | [Ru(L ₂)(Cl) ₂ (H ₂ O) ₂] | C ₂₁ H ₂₃ RuN ₄ O ₅ Cl ₂ | 579.43 | >300 | 80 | Green | 45.60 | 4.00 | 9.67 |
| | | | | | | | (47.35) | (3.52) | (7.75) |
| 3 | [Ru(L ₃)(Cl) ₂ (H ₂ O) ₂] | C ₂₁ H ₂₃ RuN ₄ O ₅ Cl ₃ | 583.85 | >300 | 75 | Dark | 43.20 | 3.45 | 9.59 |
| | | | | | | Green | (34.72) | (2.76) | (5.84) |

3.1. IR spectra

The FTIR spectra provide valuable information regarding the nature of the functional group attached to the metal atom. The IR spectral data of the ligands (HL_n) and their Ru(III) complexes (1-3) are given in Table 2. By comparing the IR spectra of ligands with those of their Ru(III) complexes, the following features can be pointed out:

The broad band due to $\nu(\text{OH})$ functionality of phenol appear in the spectra of the ligands at 3417-3445 cm^{-1} region. This band disappear in the spectra of Ru(III) complexes with appearing a medium band corresponding to $\nu(\text{C-O})$ at 1126-1130 cm^{-1} region indicating that, the ligands coordinate through their deprotonated form and formation metal-oxygen bonds [16]. The band due to $\nu(\text{NH, pyrazole})$ and $\nu(\text{N=N})$ groups which appeared in the spectra of the ligands at 3321-3335 and

1495-1498 cm^{-1} regions, respectively appeared at the same position in the spectra of their Ru(III) complexes [17], which can be taken as evidence that (NH, pyrazole) and (N=N) groups are not taking part in the coordination to the Ru center.

The bands due to $\nu(\text{C=N, pyrazole})$ group which appeared in the spectra of the ligands at 1592-1596 cm^{-1} region were shifted to lower wavenumbers by 12-21 cm^{-1} indicating their coordination to the Ru center [17]. The presence of lattice and/or coordinated water molecules in the structure of Ru(III) complexes is further supported by the appearance of broad band at 3300-3500 cm^{-1} region corresponding to $\nu(\text{OH})$ of water molecules [18]. The nature of water of crystallization rather than coordination will be discussed in the thermal analysis part.

In addition, new bands were observed in the regions 690-692 and 538-545 cm^{-1} which were assigned to the formation of Ru-O and Ru←N bonds, respectively [19].

Table 2. IR data (cm^{-1}) of free ligands (HL_n) and their Ru(III) complexes (1-3)

| Comp. | νOH | $\nu\text{H}_2\text{O}$ | νNH | $\nu\text{C=N}$ | $\nu\text{N=N}$ | $\nu\text{C-O}$ | $\nu\text{Ru-O}$ | $\nu\text{Ru-N}$ |
|-----------------|----------------|-------------------------|----------------|-----------------|-----------------|-----------------|------------------|------------------|
| HL ₁ | 3417 | ----- | 3321 | 1596 | 1495 | ----- | ----- | ----- |
| HL ₂ | 3421 | ----- | 3328 | 1592 | 1498 | ----- | ----- | ----- |
| HL ₃ | 3445 | ----- | 3335 | 1595 | 1498 | ----- | ----- | ----- |
| 1 | ----- | 3435 | 3320 | 1575 | 1495 | 1126 | 690 | 538 |
| 2 | ----- | 3440 | 3330 | 1580 | 1498 | 1130 | 692 | 540 |
| 3 | ----- | 3440 | 3335 | 1581 | 1495 | 1130 | 690 | 545 |

3.2. Electronic spectra

The electronic spectra of the complexes (Fig. 1) were recorded in dimethylformamide solvent in the range of 300-700 nm. The ground state of ruthenium(III) ion ($t_{2g}^5 e_g$ configuration) is ${}^2T_{1g}$ and the first excited doublet levels, in order of increasing energy, are ${}^2A_{2g}$ and ${}^2T_{1g}$ arising from $t_{2g}^4 e_g^1$ configuration. Bands that were observed in 586-605 nm region have been assigned to d-d transitions, while bands in the 480-510 nm region have been assigned to charge transfer transitions. These features indicate a low-spin octahedral geometry around Ru(III) ion [20].

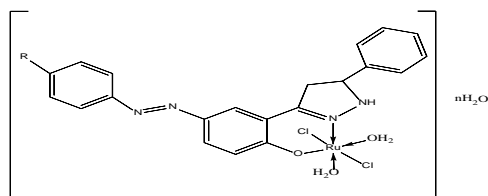


Fig. 1. Structure of Ru(III) complexes (1-3).
R= -H (1), -OCH₃ (2) and -Cl (3).

3.3. Thermal analyses

Ru(III) complexes showed TG curves in the temperature range ~100-180 °C loss of two coordinated H₂O molecules. The second stage is related to loss of the part of ligand [20]. The final weight losses are due to the decomposition of the rest of the ligand and metal oxides residue.

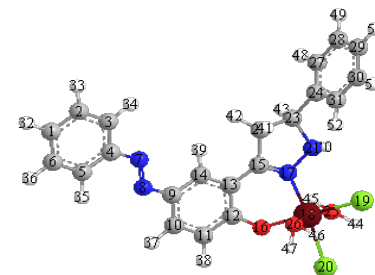
3.4. Molecular Structural

The molecular structures of the complexes (1-3) were optimized by HF method with 3-21G basis set. The molecules were built with the Perkin Elmer ChemBioDraw and optimized using Perkin Elmer ChemBio3D software. The geometrical parameters bond lengths and bond angles of Ru(III) complexes are calculated.

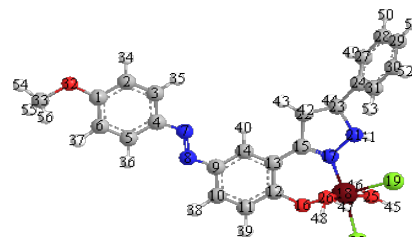
Molecular structures (HOMO & LUMO) of the complexes are presented in Fig. 2 and 3. The HOMO-LUMO energy gap, ΔE , which is an important stability index, is applied to develop theoretical models for explaining the structure and conformation barriers in many molecular systems. The smaller is the value of ΔE , the more is the reactivity of the compound has [14]. The calculated quantum chemical parameters are given in in Table 3. Additional parameters such as separation energies, ΔE , absolute electronegativities, χ , chemical potentials, P_i , absolute hardness, η , absolute softness, σ , global electrophilicity, ω , global softness, S , and additional electronic charge, ΔN_{max} , have been calculated [21].

Table 3. The calculated quantum chemical properties of Ru(III) complexes (1-3).

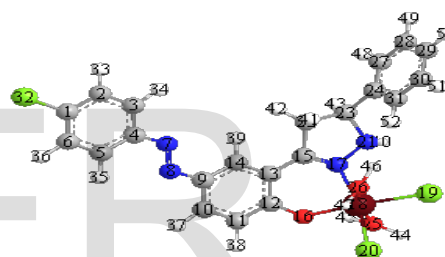
| Comp. | -E _{HOMO} (eV) | -E _{LUMO} (eV) | ΔE (eV) | χ (eV) | η (eV) | σ (eV) ⁻¹ | -P _i (eV) | S (eV) ⁻¹ | ω (eV) | ΔN_{max} (eV) |
|-------|----------------------------|----------------------------|--------------------|----------------|----------------|--------------------------------|-------------------------|-------------------------|------------------|--------------------------|
| (1) | 9.383 | 8.680 | 0.703 | 9.032 | 0.352 | 2.845 | 9.032 | 1.422 | 116.028 | 25.694 |
| (2) | 9.382 | 8.654 | 0.728 | 9.018 | 0.364 | 2.747 | 9.018 | 1.374 | 111.709 | 24.775 |
| (3) | 9.834 | 8.504 | 1.330 | 9.169 | 0.665 | 1.504 | 9.169 | 0.752 | 63.211 | 13.788 |



(1)



(2)



(3)

Fig. 2. The calculated molecular structures of Ru(III) complexes (1-3).

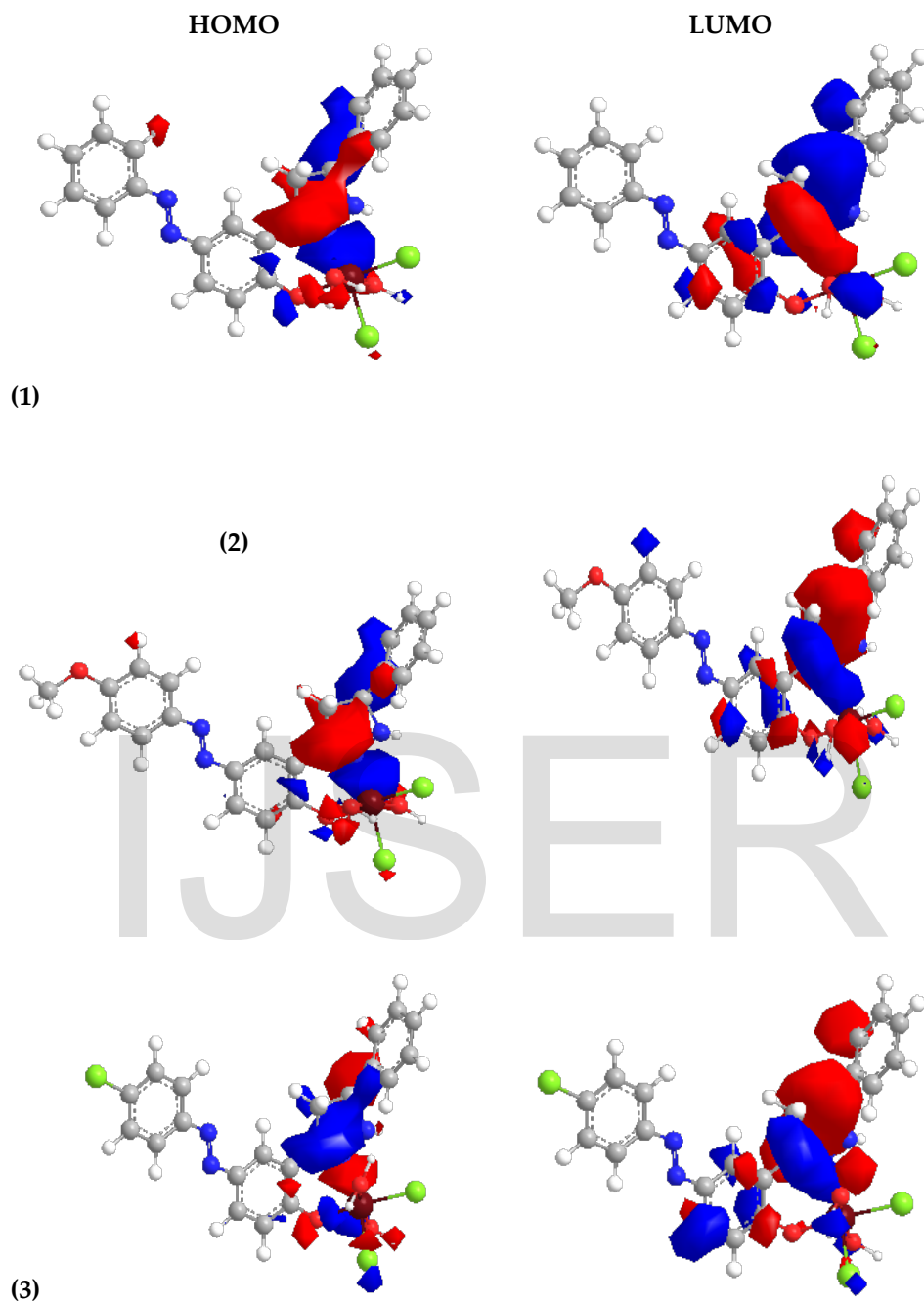


Fig. 3. The highest occupied Molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of Ru(III) complexes (1-3).

4 CONCLUSIONS

The structure of Ru(III) complexes of ligands (HL_n) were confirmed by elemental analyses, IR, molar conductance and thermal analysis data. Therefore, from IR spectrum, it is concluded that HL_n binds to the Ru(III) as a monobasic bidentate ligand by coordinating via the nitrogen atom of the pyrazole ring (-HN-N) and oxygen atom of the phenolic OH group with the displacement of the hydrogen atom from the latter group. The optimized bond lengths, bond angles and calculated the quantum chemical parameters for Ru(III) complexes were investigated.

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