

NBO Population Analysis and Electronic Calculation of Four Azopyridine Ruthenium Complexes by DFT Method

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Abstract

The molecular structure, the Natural Bond orbital (NBO) and the Time Dependent-DFT of both isomers *cis* or γ -Cl and *trans* or δ -Cl of $\text{RuCl}_2(\text{L})_2$, where L stands respectively for 2-phenylazopyridine (Azpy), 2,4-dimethyl-6-[phenylazo]pyridine (Dazpy), 2-[(3,5-dimethylphenyl)azopyridine] (Mazpy) and 2-pyridylazonaphthol (Nazpy) were calculated with DFT method at B3LYP/LANL2DZ level. The prediction of the frontier orbitals (Highest Occupied Molecular Orbital or HOMO and Lowest Unoccupied Molecular Orbital or LUMO) shows that the most active complexes suitable for electronic reactions are admitted to be the *trans* isomers. Moreover, δ - $\text{RuCl}_2(\text{Azpy})_2$ is discovered to react more actively as photo-sensitizer since its energy gap is the minimum. Besides, electronic structures of all complexes through NBO calculation indicate that Ru-N bonds are made of delocalization of occupancies from lone pair orbital of N atoms to the ruthenium. Moreover, Ru was assumed to have almost the same charge regardless the structure of the azopyridine ligands in the complex indicating that the ligands provide only a steric effect that is responsible for the ruthenium's selectivity. Concerning the transition state, NBO analysis also highlights that the transition $\text{LP}(\text{Ru}) \rightarrow \pi^*(\text{N}_1-\text{N}_2)$ does correspond to $t_{2g} \rightarrow \pi^*(\text{L})$. This transition is assumed to correspond to Metal to Ligand Charge Transfer (MLCT) that is responsible for the photo-sensitiveness of the metallic complex. Besides, TDDFT calculation of complexes showed that δ - $\text{RuCl}_2(\text{Nazpy})_2$ displays the largest band during the absorption. For that reason, it is admitted to be the best photosensitizer due to a large system of conjugation provided by Nazpy ligand.

Keywords

Natural Bond Orbital (NBO), HOMO, LUMO, Azopyridine Ligand, MLCT, LLCT

1. Introduction

Since azopyridine complexes of ruthenium have been of real interest for their capability

not merely to limit the metal degree of oxidation to II or III rendering it more selective but also to throw off cancer disease [1] [2] [3] [4], no theoretical investigation was performed to well account for their electron transfer. In our former papers, we showed up that all azopyridine ligands are bidentate e.g. they link to ruthenium by two nitrogen atoms forming then a five center stable complex [5]. We also showed that thanks to the asymmetry of ligands, five isomers are normally obtainable. But when complex is synthesized by combining $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ with any azopyridine ligand, only both isomers *cis* and *trans* are obtained as displayed by **Figure 1** [6].

We assumed therefore that by this method of synthesis, the most producible complex is up today $\gamma\text{-Cl}$. Moreover, literature explains that azopyridine complexes of ruthenium can be used as sensitizer better than bipyridine complexes of ruthenium [2]. In this work, we object to compare the reactivity of complexes when the ligand changes and investigate the nature of Ru-N bonding by using natural bond orbital (NBO) analysis since NBO is admitted to highlight the electronic structure of a molecule [7]. Moreover, through time dependent DFT (TD-DFT) we intend to find out which complex must be electronically active to behave as photo-sensitizer. Our study regards four azopyridine ligands of ruthenium named $\text{RuCl}_2(\text{Azpy})_2$, $\text{RuCl}_2(\text{Dazpy})_2$, $\text{RuCl}_2(\text{Mazpy})_2$ and $\text{RuCl}_2(\text{Nazpy})_2$ whose ligands are displayed by **Figure 2**.

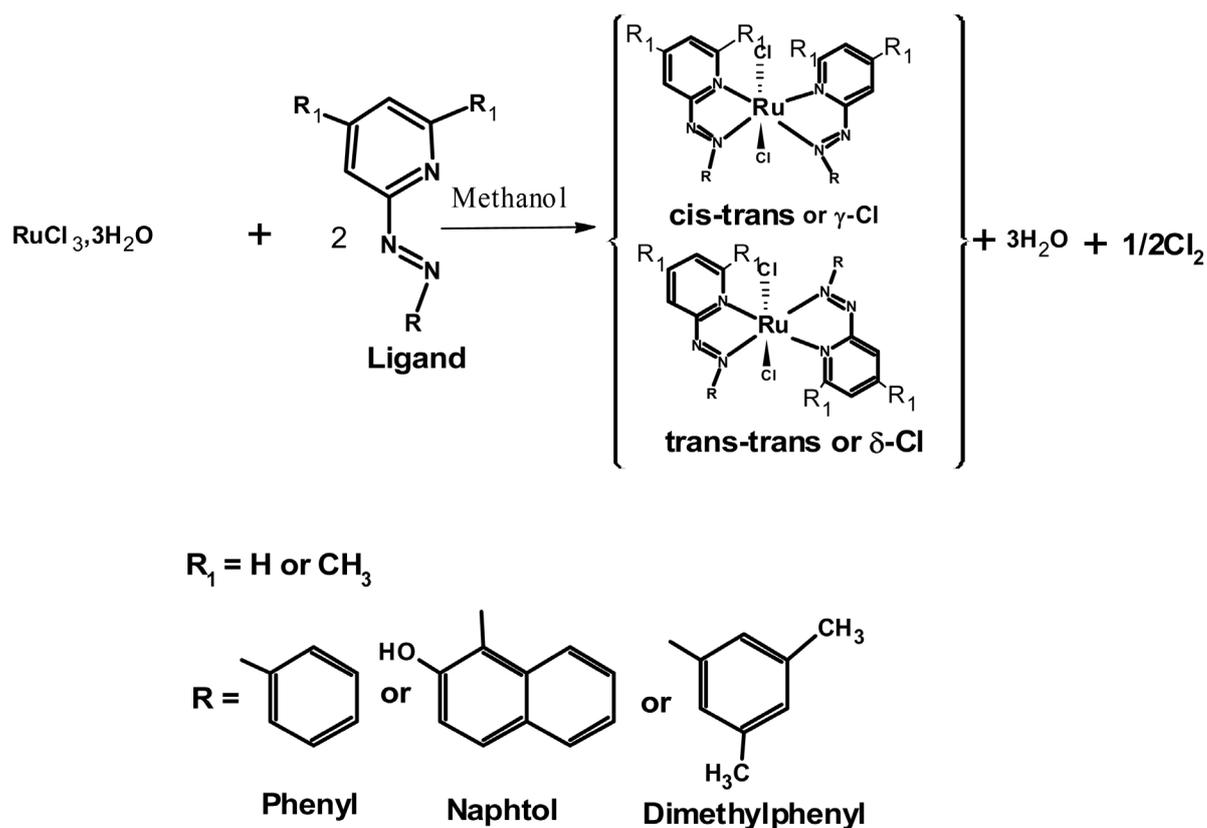


Figure 1. Synthesis of azopyridine ruthenium complexes. In this paper, azopyridine ligands were formed by combinations of both R and R_1 . Thus, when phenyl ring replaces R, and R_1 is H, then we have Azpy ligand. Nazpy ligand corresponds to R replaced by naphtol ring and R_1 by H. when R_1 is CH_3 substituent and R is phenyl ring, then we have Dazpy ligand. Whereas Mazpy, it is formed of R replaced by dimethylphenyl group and R_1 by hydrogen atom. In all structures, chlorine atoms are in trans position.

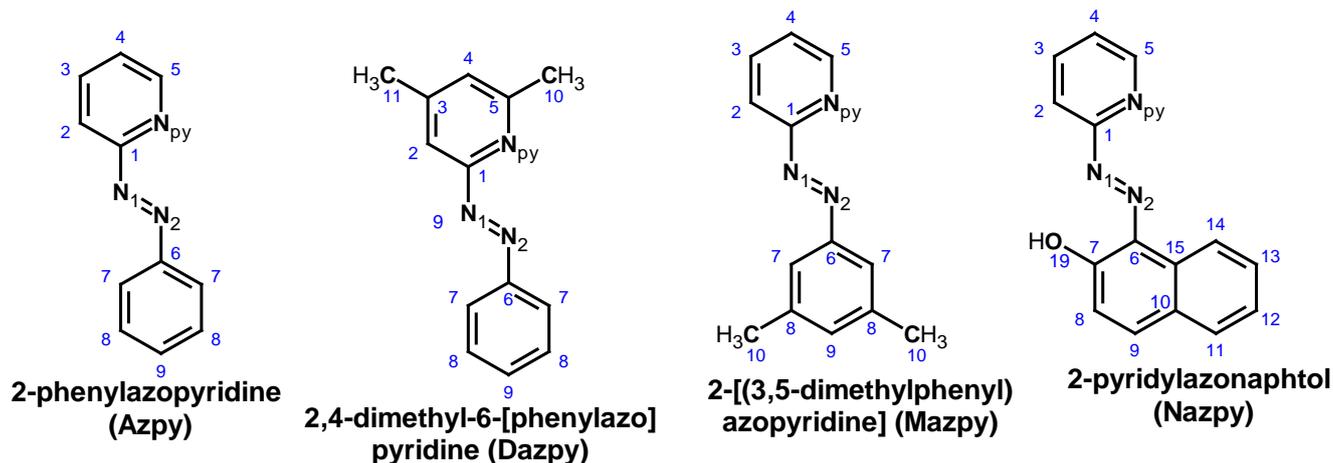


Figure 2. Azopyridine ligands involved in ruthenium complexes formations. Numbers indicate carbon atoms.

The regarding isomers are all admitted to be C_2 -symmetrical except δ - $\text{RuCl}_2(\text{Nazpy})_2$ that is C_i -symmetrical. Anyhow, they all present a C_2 axis that makes both azopyridine ligands identical within each complex [8].

2. Method

All geometry optimizations were performed with DFT method using Becke's hybrid three parameters exchange functional of non local correlation functional of Lee Yang and Parr (B3LYP). They were carried out using an effective core Lanl2dz basis set owing to the relativist effect of core electrons from ruthenium atom [9]. The resulting geometries were verified as minima by frequency calculation. NBO whose program is embedded in Gaussian 09 package used for calculations [10] [11] was developed at B3LYP/Lanl2dz level on optimized molecules. The natural bond orbital analysis emphasizes the role of intermolecular orbital interaction or charge transfer in the complex. It is performed by considering all possible interaction between filled donor and empty acceptor NBOs and estimating their energetic importance by second-order perturbation theory. The stabilization energy E_2 [12] associated with electron delocalization between electron donor NBO(i) and electron acceptor NBO(j) is evaluated according to equation below.

$$E_2 = \Delta E(ij) = q_i \frac{(F(i, j))^2}{\varepsilon_j - \varepsilon_i} = q_i \frac{F_{ij}^2}{\Delta\varepsilon} \quad (1)$$

where q_i stands for the orbital occupancy, ε_i and ε_j are diagonal elements (orbital energies) and F_{ij} is the off-diagonal NBO Fock matrix element. The Natural Localized Molecular Orbital NLMO that displays the delocalization from a Lewis orbital to a non Lewis orbital was also predicted at B3LYP/Lanl2dz level. It thus provides additional evidence of the intermolecular delocalization effects [13]. Practically, each semi-localized NLMO Ω_i is expressed as a linear combination of the parent Lewis-type NBO σ_i (with coefficient $c_{ii} \cong 1$) and residual weak contributions ($c_{ij} \cong 0$) from non-Lewis NBOs σ_j^* as indicated in Equation (2).

$$\Omega_i = c_{ii}\sigma_i + \sum_j^{NL} c_{ji}\sigma_j^* \quad (2)$$

Clearly, NLMO completes the NBO summary and the perturbation theory energy. Regarding electronic prediction, it was carried out using TDDFT method with combined basis set. Thus Ru was lonely calculated with ECP Lanl2dz while the remaining atoms were performed with polarized split valence 6-31G(d) basis set.

3. Results and Discussions

3.1. Frontier Molecular Orbital Energies

The frontier molecular orbitals comprising the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) with the energy gap between HOMO and LUMO (ΔE) of the complexes are calculated and displayed in **Table 1**. Frontier orbital highlights the reactive property of complexes. The HOMO is the first orbital provider of the electron and the LUMO is the first orbital acceptor of the electron, and the gap between HOMO and LUMO characterizes the molecular chemical stability. The energy gap between the HOMO and the LUMO molecular orbitals is a critical parameter in determining molecular electrical transport properties though it is a measure of electron conductivity [14]. The chemical activity of the molecule is also observed from Eigen values of LUMO and HOMO and from the energy gap value calculated from them. Thus, ΔE is the result of a significant degree of intermolecular charge transfer (ICT) from the electron donor to the efficient electron acceptor group. Besides, from HOMO and LUMO which are admitted to be respectively the ionization potential and the affinity energy, the chemical hardness was determined according to Koopman's theory given by:

$$\eta = \frac{I_p - E_A}{2} = \frac{E_{\text{LUMO}} - E_{\text{HOMO}}}{2} \quad (3)$$

where $I_p = -E_{\text{HOMO}}$ is ionization potential ($\text{Kcal}\cdot\text{mol}^{-1}$), $E_A = -E_{\text{LUMO}}$ is electronic affinity ($\text{Kcal}\cdot\text{mol}^{-1}$).

The hardness emphasizes the reactivity of the complex. Therefore, the larger the gap between HOMO and LUMO is, the harder the molecule is and the worse its reactivity is. In contrary, the chemical softness that is defined as the inverse of hardness highlights the capacity of an atom or group of atoms to receive electrons. Therefore, the soft molecule needs small energy to liberate an electron from HOMO since the gap ΔE is narrow. Besides, the chemical potential was calculated to account for the capability for

Table 1. Frontier orbital energies characterizing the reactivity of azopyridine ruthenium complexes in $\text{kcal}\cdot\text{mol}^{-1}$ calculated at B3LYP/LANL2DZ level.

	RuCl ₂ (Azpy) ₂		RuCl ₂ (Dazpy) ₂		RuCl ₂ (Mazpy) ₂		RuCl ₂ (Nazpy) ₂		RuCl ₃ ·3H ₂ O
	γ -Cl	δ -Cl	γ -Cl	δ -Cl	γ -Cl	\square δ -Cl	\square γ -Cl	\square δ -Cl	
HOMO	-123.6	-121.0	-121.6	-118.6	-126.6	-122.3	-128.0	-130.5	-153.2
LUMO	-77.2	-79.5	-70.9	-74.7	-75.6	-78.4	-82.2	-86.0	-95.7
ΔE^a	46.4	41.5	50.7	43.9	51.0	43.9	45.8	44.5	57.5
η	-23.2	-20.75	-25.3	-21.9	-25.5	-21.9	-22.9	-22.2	-28.7
μ	-100.4	-100.25	-96.2	-96.6	-101.1	-100.3	-105.1	-108.2	-124.4

^a $\Delta E = \text{LUMO} - \text{HOMO}$.

electron to leave from the molecule through Equation (3) as:

$$\mu = \frac{I_p + E_A}{2} \quad (4)$$

In **Table 1**, we can well see with each complex that the most reactive isomer represents δ -Cl for which energy gap is small. This can certainly be explained by the fact that both ligands are in *Trans* position where the repulsion brought about by the steric effect between them is minimized. Moreover, and specifically, δ -RuCl₂(Azpy)₂ is the most reactive complex with 41.5 Kcal·mol⁻¹. In consequence, it is assumed to be the soft molecule though it displays the low value of hardness [15]. However, the reactive RuCl₃·3H₂O presents the highest energy gap with 57.5 Kcal·mol⁻¹. Therefore, it is admitted to be the hardest molecule.

3.2. NBO Analysis

The natural bond orbital was performed on complexes using the pseudo-potential LANL2DZ basis set whose particularity is to freeze the core electrons [16] within the ruthenium atom. Therefore, **Table 2** displays the electronic structure of ruthenium for each of the complexes. The calculations were made on the complexes, the reactive RuCl₃·3H₂O and also on ruthenium atom.

According to NBO analysis, **Table 2** shows up that the structure of the valence orbital of Ru is characterized by 4d5s. Regarding the core electrons, **Table 3** shows that LANL2DZ provides approximately 36 electrons regardless the structure of the ligand. Whereas the Rydberg orbitals (5p5d6p), they account for the more extended bits of the bases functions used including polarization functions electrons. Their occupancies within the complexes are low and constant with 0.06 electrons except Ru atom that does not display any value. We can assume that the Rydberg electrons are certainly related to the presence of ligands. Almost the same remark concerns the valence electrons where only Ru atom displays 8 electrons while all complexes show almost 7.40 electrons. Regarding the total electrons in ruthenium atom that is 44 when it is isolated, RuCl₂(L)₂ complexes display almost a constant value of 43.44 electrons while RuCl₃·3H₂O displays 43.1 electrons. Consequently, we can admit that these results tend to highlight the electron donor's strength of azopyridine ligands to Ru. In reality, the nominal

Table 2. Electronic structure of ruthenium undergoing the pseudo-potential effect to minimize the relativistic effect.

γ -RuCl ₂ (Azpy) ₂	[core] 5s(0.28) 4d(7.12) 5p(0.01) 5d(0.03) 6p(0.02)
δ -RuCl ₂ (Azpy) ₂	[core] 5s(0.27) 4d(7.14) 5p(0.01) 5d(0.03) 6p(0.02)
γ -RuCl ₂ (Dazpy) ₂	[core] 5s(0.28) 4d(7.12) 5p(0.01) 5d(0.03) 6p(0.02)
δ -RuCl ₂ (Dazpy) ₂	[core] 5s(0.27) 4d(7.12) 5p(0.1) 5d(0.03) 6p(0.02)
γ -RuCl ₂ (Mazpy) ₂	[core] 5s(0.27) 4d(7.10) 5p(0.01) 5d(0.03) 6p(0.02)
δ -RuCl ₂ (Mazpy) ₂	[core] 5s(0.27) 4d(7.13) 5p(0.01) 5d(0.03) 6p(0.02)
γ -RuCl ₂ (Nazpy) ₂	[core] 5s(0.27) 4d(7.14) 5p(0.1) 5d(0.03) 6p(0.02)
δ -RuCl ₂ (Nazpy) ₂	[core] 5s(0.27) 4d(7.16) 5p(0.01) 5d(0.03) 6p(0.02)
Ru atom	[core] 5s(0.49) 4d(7.51)
RuCl ₃ ·3H ₂ O	[core] 5s(0.28) 4d(6.77) 5p(0.02) 5d(0.03) 6p(0.01)

Table 3. Allotment of ruthenium electrons between core, valence and Rydberg orbitals.

	Core	Valence	Rydberg	Total
γ -RuCl ₂ (Azpy) ₂	35.98	7.40	0.06	43.44
δ -RuCl ₂ (Azpy) ₂	35.98	7.40	0.06	43.44
γ -RuCl ₂ (Dazpy) ₂	35.98	7.40	0.06	43.44
δ -RuCl ₂ (Dazpy) ₂	35.98	7.39	0.06	43.43
γ -RuCl ₂ (Mazpy) ₂	35.98	7.37	0.06	43.41
δ -RuCl ₂ (Mazpy) ₂	35.98	7.40	0.06	43.44
γ -RuCl ₂ (Nazpy) ₂	35.98	7.41	0.06	43.45
δ -RuCl ₂ (Nazpy) ₂	35.98	7.42	0.06	43.46
Ru atom	36.00	8.00	0.00	44.00
RuCl ₃ ·3H ₂ O	36.00	7.04	0.06	43.10

charge of Ru in RuCl₂(L)₂ is +2. So, the natural atomic charge that corresponds to the difference between the nuclear charge of Ru (44) and its total electron population in **Table 3** within each complex is very low (lower than +2) confirming a significant transfer of electron density from the ligands to Ru [17]. However, regarding RuCl₃·3H₂O, the nominal charge of Ru is +3 due to the presence of three chloride atoms while the natural charge is +0.9. This discrepancy of charge is attributed to the presence of water molecules that are known to be strong electrons donors.

Table 4 displays the atomic charges for each atom involved in the formation of Ru-Ligand bonds. It shows that the charge of Ru in the complex is almost the same regardless both the nature of the ligand and the configuration of the complex's isomer [2] [18]. Thus, we can admit that azopyridine ligands behave seemingly and the hindrance that they provide should have no electronic influence on the charge of Ru. However, it must certainly induce a steric effect necessary for selective reactions [6] and for the symmetry. For instance, while the three complexes δ -RuCl₂(Azpy)₂, δ -RuCl₂(Dazpy)₂ and δ -RuCl₂(Mazpy)₂ are C₂-symmetrical with different chloride atoms, δ -RuCl₂(Nazpy)₂ presents a C_i symmetry indicating an inversion center [19]. Herein, all ligands are consequently identical by pairs and thus, symmetric atoms display the same charge. Regarding the charges of nitrogen atoms both on ligands (**Table 5**) and on ruthenium complexes (**Table 4**), the lowest charges are located on both N₁ and N_{py}. Therefore, since the azopyridine ligands are known to be bidentate structures [5], we can believe that the electrons density on N₁ should be delocalized either on N_{py} or on N₂ that leads to the formation of Ru-N_{py} and Ru-N₂ bonds. This process will give then rise to a five-ring stable shape of complex [5] [20]. **Table 6**, displays the interaction between N₁, N₂ and N_{py} atoms through NLMO delocalization of N₁ electrons within the four azopyridine ligands.

Through **Table 6**, we can see that the four ligands delocalize the occupancies of the lone pair LP(N₁) in the same natural atomic orbitals NAOs. Principally, LP(N₁) delocalizes greatly onto the C₁-N_{py} antibond. This fact confirms the identical electronic behavior of the azopyridine ligands.

Table 4. The NBO atomic charges of atoms involved in formation of Ru-Ligand bonds within azopyridine complexes of ruthenium calculated at B3LYP /Lan12dz level.

Atoms	RuCl ₂ (Azpy) ₂		RuCl ₂ (Dazpy) ₂		RuCl ₂ (Mazpy) ₂		RuCl ₂ (Nazpy) ₂	
	γ -Cl	δ -Cl	γ -Cl	δ -Cl	γ -Cl	δ -Cl	γ -Cl	δ -Cl
Ru	0.55	0.55	0.56	0.57	0.59	0.55	0.55	0.53
N ₁	-0.25	-0.22	-0.24	-0.22	-0.23	-0.20	-0.22	-0.20
N ₂	-0.16	-0.16	-0.15	-0.18	-0.17	-0.16	-0.19	-0.18
N _{py}	-0.48	-0.46	-0.52	-0.50	-0.47	-0.46	-0.47	-0.47
Cl ₁	-0.52	-0.54	-0.53	-0.54	-0.51	-0.53	-0.51	-0.51
Cl ₂	-0.52	-0.52	-0.53	-0.53	-0.51	-0.53	-0.51	-0.51

Table 5. The NBO atomic charges of nitrogen atoms of azopyridine ligands involved in ruthenium complex formation at B3LYP/Lan12dz level.

Atoms	Azpy	Dazpy	Mazpy	Nazpy
N _{py}	-0.48	-0.51	-0.49	-0.49
N ₁	-0.26	-0.26	-0.26	-0.28
N ₂	-0.18	-0.18	-0.19	-0.17

Table 6. Linear combination of NBO LP(N_i) in each ligand with the parent Lewis LP(N_i) and non Lewis orbitals in which its electrons can delocalize through NLMO analysis. The predictions were performed at B3LYP/Lan12dz level.

Azpy	$\sigma = 97.79\% \sigma(N_1) + 0.80\% sp^{5.26}(C_1) + 0.21\% sp^{1.32}(N_2) + 0.35\% sp^{0.97}(N_{py})$
Dazpy	$\sigma = 97.74\% \sigma(N_1) + 0.86\% sp^{5.62}(C_1) + 0.19\% sp^{1.56}(N_2) + 0.38\% sp^{1.13}(N_{py})$
Mazpy	$\sigma = 97.19\% \sigma(N_1) + 0.98\% sp^{7.22}(C_1) + 0.25\% sp^{1.67}(N_2) + 0.45\% sp^{1.91}(N_{py})$
Nazpy	$\sigma = 96.97\% \sigma(N_1) + 1.064\% sp^{8.02}(C_1) + 0.23\% sp^{2.08}(N_2) + 0.49\% sp^{2.08}(N_{py})$

The NBO Occupancy within the Ru Complexes

All azopyridine complexes studied herein are admitted to show a C₂ axis [19]. So, both azopyridine ligands (ref. **Figure 1**) are identical and nitrogen atoms involved in the formation of Ru-ligand bonds are assumed to be in the same environment by pair. Regarding both chlorine atoms, they covalently bind to Ru atom since its nominal charge is +II. Here, the occupancy of NBO was performed at B3LYP/Lan12dz level. So, **Table 7** and **Table 8** list the calculated occupancies of natural orbitals and natural hybrids of several atoms involved in the formation of Ru-N bonds in RuCl₂(L)₂ comprising electron delocalization. L stands for 2-phenylazopyridine (Azpy), 2-phenylazo-4,6-dimethylpyridine (Dazpy), 2,6-dimethylphenylazo-2-pyridine (Mazpy) and 2-pyridylazonaphthol (Nazpy). In these aforementioned Tables, only the AOs that occupancies are far lower than the ideal occupancy (2.0e) and the MOs involved in electronic transition are presented. It is assumed that the low occupancies of an AO disclose the orbital to be involved in MO formation [21].

With azopyridine ligands and according to the reactive RuCl₃·3H₂O, ruthenium is involved in an octahedral structure with six single bonds. Regarding RuCl₂(L)₂, Cl atoms that are responsible for the nominal charge +II of Ru are involved in an ionic

Table 7. Occupancy of natural orbitals (NBOs) and hybrids on Cl, N and Ru atoms involved in formation of Ru-Ligand in γ - and δ -RuCl₂(L)₂ at B3LYP/LANL2DZ level.

Donor Lewis-type ^a NBO (Ru-N)	Occupancy	Hybrid ^b	AO(c) ^c	AO(%) ^d
γ -RuCl ₂ (Azpy) ₂				
LP(N _i)	1.93	sp ^{1.5}	0.63(2s) + 0.62(2p _y) - 0.46(2p _z)	s(40.03%)p(59.97%)
LP(N ₂)	1.66	sp ^{1.68}	0.61(2s) + 0.63(2p _y) + 0.48(2p _z)	s(37.34%)p(62.66%)
LP(N _{py})	1.68	sp ^{2.75}	0.52(2s) + 0.72(2p _y) - 0.46(2p _z)	s(26.69%)p(73.31%)
LP(Ru)	1.59	d ^{99.99}	0.37(4d _{z²}) - 0.92(4d _{xy}) - 0.10(4d _{x²-y²})	s(0.03%)d(99.97%)
LP*(Ru)	0.84	pd ^{99.99}	0.99(4d _{yz}) + 0.15(4d _{xz})	p(0.02%)d(99.98%)
δ -RuCl ₂ (Azpy) ₂				
LP(N _{py})	1.68	sp ^{2.64}	0.52(2s) - 0.77(2p _x) - 0.25(2p _y) + 0.25(2p _z)	s(27.48%)p(72.52%)
LP(N ₂)	1.68	sp ^{1.65}	0.61(2s) + 0.50(2p _x) - 0.61(2p _y)	s(37.78%)p(62.22%)
LP(N _i)	1.94	sp ^{1.52}	0.63(3s) + 0.50(2p _x) - 0.59(2p _y)	s(39.66%)p(60.34%)
LP(Ru)	1.58	d ¹⁰⁰	0.88(4d _{xz}) - 0.47(4d _{yz})	p(0.01%)d(99.99%)
LP*(Ru)	0.80	d ¹⁰⁰	0.18(4d _{z²}) - 0.88(4d _{xy}) - 0.43(4d _{x²-y²})	s(0.39%)d(99.61%)
γ -RuCl ₂ (Dazpy) ₂				
LP(N _{py})	1.69	sp ^{2.73}	0.52(2s) + 0.70(2p _y) - 0.21(2p _y) - 0.44(2p _z)	s(26.82%)p(73.18%)
LP(N ₂)	1.65	sp ^{1.69}	0.60(2s) + 0.60(2p _x) + 0.18(2p _y) + 0.49(2p _z)	s(37.17%)p(62.83%)
LP(N _i)	1.93	sp ^{1.52}	0.63(2s) + 0.59(2p _x) + 0.20(2p _y) - 0.47(2p _z)	s(39.75%)p(60.25%)
LP(Ru)	1.61	d ¹⁰⁰	0.83(4d _{xy}) - 0.23(4d _{x²-y²}) + 0.5(4d _{z²})	s(0.03%)d(99.97%)
LP*(Ru)	0.92	d ¹⁰⁰	0.90(4d _{x²-y²}) - 0.42(4d _{z²})	s(0.31%)d(99.69%)
δ -RuCl ₂ (Dazpy) ₂				
LP(N _{py})	1.68	sp ^{2.67}	0.52(2s) - 0.84(2p _x) - 0.11(2p _y)	s(27.28%)p(72.72%)
LP(N ₂)	1.68	sp ^{1.62}	0.62(2s) + 0.22(2p _x) + 0.69(2p _y) + 0.30(2p _z)	s(38.14%)p(61.86%)
LP(N _i)	1.93	sp ^{1.53}	0.63(2s) + 0.22(2p _x) + 0.70(2p _y) - 0.27(2p _z)	s(39.47%)p(60.53%)
LP(Ru)	1.56	d ¹⁰⁰	0.89(4d _{yz}) - 0.46(4d _{xz})	p(0.02%)d(99.98%)
LP*(Ru)	0.79	d ¹⁰⁰	0.23(4d _{z²}) + 0.26(4d _{xy}) - 0.94(4d _{x²-y²})	s(0.26%)p(0.01%)d(99.73%)
γ -RuCl ₂ (Mazpy) ₂				
LP(N _{py})	1.67	sp ^{2.77}	0.51(2s) + 0.72(2p _y) - 0.46(2p _z)	s(26.54%)p(73.46%)
LP(N ₂)	1.67	sp ^{1.56}	0.63(2s) - 0.11(2p _x) + 0.63(2p _y) + 0.44(2p _z)	s(39.12%)p(60.88%)
LP(N _i)	1.93	sp ^{1.48}	0.63(2s) + 0.63(2p _y) - 0.44(2p _z)	s(40.36%)p(59.64%)
LP(Ru)	1.64	d ¹⁰⁰	- 0.95(4d _{xy}) - 0.20(4d _{x²-y²}) + 0.22(4d _{z²})	d(100%)
LP*(Ru)	0.84	d ^{99.99}	0.99(4d _{yz}) + 0.13(4d _{xz})	p(0.01%)p(99.99%)
δ -RuCl ₂ (Mazpy) ₂				
LP(N _{py})	1.67	sp ^{2.73}	0.52(2s) + 0.25(2p _x) - 0.81(2p _y)	s(26.81%)p(73.19%)
LP(N ₂)	1.68	sp ^{1.55}	0.63(2s) - 0.77(2p _y)	s(39.21%)p(60.79%)
LP(N _i)	1.93	sp ^{1.53}	0.63(2s) - 0.77(2p _x)	s(40.06%)p(59.94%)
LP(Ru)	1.60	d ¹⁰⁰	0.92(4d _{xz}) - 0.40(4d _{yz})	d(100%)
LP*(Ru)	0.82	d ^{99.99}	0.17(4d _{xy}) + 0.98(4d _{x²-y²})	s(0.27%)d(99.73%)
γ -RuCl ₂ (Nazpy) ₂				
LP(N _{py})	1.66	sp ^{2.78}	0.51(2s) + 0.68(2p _x) - 0.21(2p _y) - 0.47(2p _z)	s(26.44%)p(73.56%)
LP(N ₂)	1.68	sp ^{1.71}	0.61(2s) + 0.64(2p _x) + 0.47(2p _z)	s(36.85%)p(63.15%)

Continued

LP(N _i)	1.93	sp ^{1.47}	0.64(2s) + 0.63(2p _x) - 0.44(2p _z)	s(40.42%)p(59.58%)
LP(Ru)	1.62	d ¹⁰⁰	0.71(4d _{xy}) + 0.62(4d _{x²-y²) + 0.33(4d_{z²})}	d(100%)
LP*(Ru)	0.90	d ^{99.99}	0.70(4d _{xy}) - 0.57(4d _{x²-y²) - 0.42(4d_{z²})}	s(0.31%)p(99.69%)
δ -RuCl ₂ (Nazpy) ₂				
LP(N _{py})	1.68	sp ^{2.72}	0.52(2s) - 0.21(2p _x) + 0.82(2p _z)	s(26.88%)p(73.12%)
LP(N ₂)	1.68	sp ^{1.67}	0.61(2s) + 0.11(2p _x) - 0.71(2p _y) - 0.33(2p _z)	s(37.41%)p(62.59%)
LP(N _i)	1.94	sp ^{1.51}	0.63(2s) - 0.15(2p _x) + 0.68(2p _y) + 0.33(2p _z)	s(39.90%)p(60.10%)
LP(Ru)	1.61	d ¹⁰⁰	0.46(4d _{xy}) + 0.53(4d _{xz}) + 0.20(4d _{yz}) - 0.63(4d _{x²-y²) + 0.26(4d_{z²})}	d(100%)
LP*(Ru)	0.81	d ^{99.99}	0.22(4dyz) - 0.26(4d _{xy}) + 0.52(4d _{yz}) - 0.16(4d _{x²-y²) - 0.76(4d_{z²})}	s(0.34%)d(99.66%)

^aLP represents Lone Pair Orbital; ^bHybrid concerns the first atom of the bond; ^cLinear combination of NAOs of the atom concerned in the NBO hybrid; ^dPercentage contribution of each NAO in the NBO hybrid.

Table 8. Second-order interaction energy (E₂, kcal/mol) between donor and acceptor orbitals in RuCl₂(L)₂ complexes at B3LYP/LANL2DZ level.

Donor→acceptor ^a	E ₂	E(j)-E(i)	F(i,j)	Donor*acceptor ^a	E ₂	E(j)-E(i)	F(i,j)
γ -RuCl ₂ (Azpy) ₂				δ -RuCl ₂ (Azpy) ₂			
□(N ₁ -N ₂)→π*(C ₁ -N _{py})	16.23	0.33	0.074	π(N ₁ -N ₂)→π*(C ₁ -N _{py})	12.40	0.39	0.066
LP(N ₂)→LP*(Ru)	80.2	0.28	0.155	LP(N ₂)→LP*(Ru)	63.49	0.30	0.141
LP(N _{py})→LP*(Ru)	76.5	0.22	0.135	LP(N _{py})→LP*(Ru)	75.21	0.24	0.137
LP(Ru)→π*(N ₁ -N ₂)	12.8	0.14	0.038	LP(Ru)→π*(N ₁ -N ₂)	14.07	0.14	0.04
γ -RuCl ₂ (Dazpy) ₂				δ -RuCl ₂ (Dazpy) ₂			
□(N ₁ -N ₂)→π*(C ₁ -N _{py})	15.70	0.034	0.074	π(N ₁ -N ₂)→π*(C ₁ -N _{py})	12.25	0.39	0.066
LP(N ₂)→LP*(Ru)	82.43	0.28	0.157	LP(N ₂)→LP*(Ru)	53.91	0.30	0.13
LP(N _{py})→LP*(Ru)	65.83	0.21	0.123	LP(N _{py})→LP*(Ru)	73.16	0.24	0.134
LP(Ru)→π*(N ₁ -N ₂)	12.77	0.14	0.038	LP(Ru)→π*(N ₁ -N ₂)	18.28	0.14	0.045
γ -RuCl ₂ (Mazpy) ₂				δ -RuCl ₂ (Mazpy) ₂			
□(N ₁ -N ₂)→π*(C ₁ -N _{py})	15.52	0.33	0.073	π(N ₁ -N ₂)→π*(C ₁ -N _{py})	13.73	0.33	0.069
LP(N ₂)→LP*(Ru)	75.9	0.29	0.152	LP(N ₂)→LP*(Ru)	74.76	0.29	0.153
LP(N _{py})→LP*(Ru)	72.47	0.23	0.132	LP(N _{py})→LP*(Ru)	71.16	0.23	0.133
LP(Ru)→π*(N ₁ -N ₂)	10.10	0.15	0.035	LP(Ru)→π*(N ₁ -N ₂)	13.27	0.14	0.039
γ -RuCl ₂ (Nazpy) ₂				δ -RuCl ₂ (Nazpy) ₂			
□(N ₁ -N ₂)→π*(C ₁ -N _{py})	15.74	0.33	0.073	π(N ₁ -N ₂)→π*(C ₁ -N _{py})	11.87	0.39	0.065
LP(N ₂)→LP*(Ru)	72.59	0.28	0.147	LP(N ₂)→LP*(Ru)	54.05	0.30	0.130
LP(N _{py})→LP*(Ru)	79.80	0.23	0.136	LP(N _{py})→LP*(Ru)	83.44	0.24	0.144
LP(Ru)→π*(N ₁ -N ₂)	9.72	0.15	0.034	LP(Ru)→π*(N ₁ -N ₂)	13.15	0.14	0.040

^aStared label (*) indicates anti-bonding, LP (A) is a valence lone pair orbital on atom A.

bonding. Therefore, σ (Ru-Cl) is a strong bond. Whereas Ru-N bonds, they are actually formed of electron transfer from lone pair LP(N) to Ru atom. **Table 7** displays the structures of LP(N) orbital expected to bind to Ru atomic orbital owing to their low occupancies. We can see that LP(N_{py}) and LP(N₂) have almost identical populations indicating their equal ability to form Ru-N bond and confirming therefore the bidentate

state of the ligands. These interactions are highlighted through **Table 8** by the second order perturbation theory where higher energies reflect the stability of the donor-acceptor interactions. Here, **Table 8** displays in fact the electron delocalization (ED) from filled donor orbital to empty acceptor orbital.

Besides, both transitions $LP(N_2) \rightarrow LP^*(Ru)$ and $LP(N_{py}) \rightarrow LP^*(Ru)$ show that only N_{py} and N_2 are involved in bonding with the same $LP^*(Ru)$ orbital.

Moreover, **Table 7** shows $LP(N_1)$ with 1.94e as occupancy. This carries out its non involvement in Ru-N bondings. However, it delocalizes its electrons in the C_1-N_{py} bonding as confirmed by **Table 6** and **Table 8**.

Whereas $LP(Ru) \rightarrow \pi^*(N_1-N_2)$, it indicates the electron delocalization regarding the metal to ligand charge transfer (MLCT) transition $t_{2g} \rightarrow \pi^*$. This result is consistent with literature where Azopyridine ligands are admitted to be π -acceptor and σ -donor [11]. This transition is also consistent with the ability for δ -Cl complexes to better behave as photo-sensitizer though the structure of their donor $LP(Ru)$ is exclusively made of combination of d_{xz} and d_{yz} as indicated in **Table 7**.

3.3. TDDFT Analysis

TD-DFT is performed to understand the electronic absorption and find out the ability for the complex to behave as sensitizer [22]. Since an efficient photosensitizer shows a strong absorption band in the visible region (400 - 800 nm) [23], **Figure 3** shows up the electronic spectra of azopyridine ruthenium complexes. We can see here that δ -Cl isomers present the highest and the widest wavelengths. Therefore, **Table 9** lists the calculated wavelengths of the complexes.

Table 9 displays the main wavelengths (λ_{max}) calculated for each complex, their excited energy, the frontier orbital's composition and the main transitions regarding the

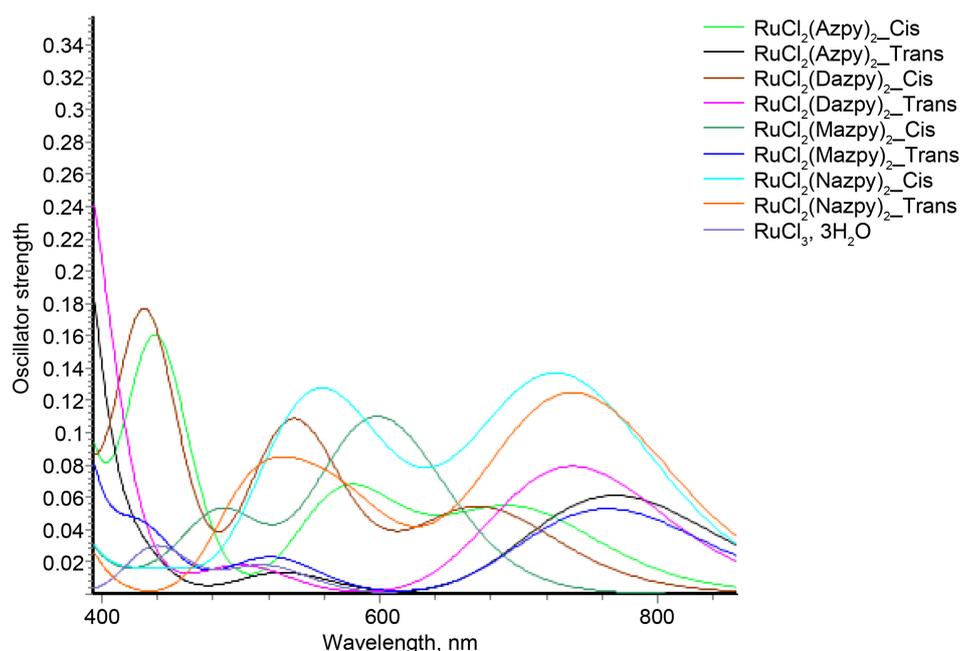


Figure 3. Simulated absorption spectra of both isomers γ -Cl and δ -Cl of azopyridine complexes including reactive $RuCl_3 \cdot 3H_2O$ recorded from 400 to 800 nm.

Table 9. Absorption properties of complexes comprising the maximum wavelength, oscillation frequency f and the main transitions involved by the energy.

Complexes	Composition of frontier orbitals		$\Delta E(\text{eV})$	λ_{max} (nm)	f	Main transition
	HOMO	LUMO				
			1.78	697.7	0.052	H→L+1 (48%)
$\gamma\text{-RuCl}_2(\text{Azpy})_2$	Ru (55%)	Azpy (86%)	2.15	577.8	0.066	H-2→L (65%)
			2.83	438.2	0.153	H-3→L (62%)
$\delta\text{-RuCl}_2(\text{Azpy})_2$	Ru (61%)	Azpy (93%)	1.61	768.7	0.061	H-1→L (70%)
			1.85	671.0	0.053	H→L+1 (49%)
$\gamma\text{-RuCl}_2(\text{Dazpy})_2$	Ru (55%)	Dazpy (87%)	2.30	537.9	0.109	H-2→L (48%)
			2.89	429.1	0.111	H-3→L (48%)
$\delta\text{-RuCl}_2(\text{Dazpy})_2$	Ru (61%)	Dazpy (94%)	1.68	738.4	0.079	H-2→L (69%)
$\gamma\text{-RuCl}_2(\text{Mazpy})_2$	Ru (54%)	Mazpy (83%)	2.00	620.4	0.053	H-2→L (43%)
			2.12	583.9	0.068	H-3→L (6%)
$\delta\text{-RuCl}_2(\text{Mazpy})_2$	Ru (59%)	Mazpy (92%)	1.62	763.2	0.053	H-1→L (70%)
$\gamma\text{-RuCl}_2(\text{Nazpy})_2$	Nazpy (97%)	Nazpy (90%)	1.68	737.8	0.104	H→L (69%)
			2.30	538.2	0.050	H-6→L (48%)
			1.62	748.1	0.106	H-1→L (68%)
$\delta\text{-RuCl}_2(\text{Nazpy})_2$	Ru (67%)	Mazpy (95%)	2.17	572.0	0.055	H-4→L (56%)
			2.41	515.3	0.061	H-2→L (69%)
$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$	Ru (60%)	Ru (70%)	2.00	516.8	0.061	H-2→L (98%)

visible region. Through this table we can see that $\gamma\text{-RuCl}_2(\text{Nazpy})_2$ presents the highest wavelength with the important extinction coefficient ($\lambda_{\text{max}} = 748.1$ nm and $f = 0.106$). We can assume that it should be the most sensitive complex. Moreover, all except one of them show that from the HOMO orbital until HOMO-4, molecular orbitals MOs are made principally of Ru orbital. Therefore, the regarding transitions are assumed to be metal to ligand charge transfer (MLCT) types. However, with $\gamma\text{-RuCl}_2(\text{Nazpy})_2$, although maximum wavelength and extinction coefficient are also slightly important, HOMO is mainly made of ligand Nazpy orbital indicating that this transition is a ligand to ligand charge transfer (LLCT) type, which is not suitable for photochemical characterisation since azopyridine ligands are reportedly insulator [6]. However, HOMO-1 is made of 63% Ru orbital and the second most important transition which wavelength is 538.2 nm with excited energy that is 2.3 eV is from H-6 to L. In consequence, we can assume that $\gamma\text{-RuCl}_2(\text{Nazpy})_2$ is not sufficiently active as sensitizer. Besides, regarding LUMO and LUMO + 1 orbitals, they are exclusively made of Ligand orbitals in all complexes. Whereas the reactive $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, its HOMO and LUMO are both made of Ru orbitals and the maximum wavelength and oscillation strength f regarding transitions are low ($\lambda_{\text{max}} = 515.3$ nm and $f = 0.061$). Since $\Delta E = 57.5$ kcal·mol⁻¹, we can see here the importance of ligands that improve the sensitivity of the ruthenium. Regarding excitation energy, we observe that $\delta\text{-RuCl}_2(\text{Azpy})_2$ presents the lowest value confirming its softness. Whereas the $\delta\text{-RuCl}_2(\text{Nazpy})_2$ it displays many metallic orbitals involved in the transition such as H-1, H-2 and H-4 with a large band of absorption. This strength

can be attributed to the larger conjugate system that the ligand Nazpy provides [24].

4. Conclusion

Four azopyridine complexes of ruthenium were predicted in this paper by NBO and TD calculations with DFT method. In order to recover the relativistic effect due to ruthenium atom, the pseudo-potential Lanl2dz basis set was used to perform calculation. Frontier molecular orbital energies calculation show first and foremost that δ -RuCl₂(Azpy)₂ is the most sensitive and soft complex expected to be used as sensitizer in photochemistry. Besides, the calculation shows that Ru atom in all complexes displays almost the same charge comprised between +0.53 and +0.59 that is significantly different from the nominal charge +2. This decrease in charge shows that azopyridine ligands are strong electrons donors. Nevertheless, the constant charge of ruthenium highlights that azopyridine ligands electronically behave similarly and the difference between them must be a steric effect for selective reactions. Furthermore, a natural bond orbital NBO analysis performed at B3LYP/Lanl2dz indicates that Ru-N bondings are made of delocalization of occupancies from Lone Pair atomic orbital of N₂ and N_{py} to Ru. Moreover, as N₁ does not link to ruthenium, it is assumed to delocalize its occupancies either in N₂ or in N_{py}. This fact confirms the bidentate structure of azopyridine ligands. In addition, NBO shows that the transition regarding LP(Ru)→π*(N₁-N₂) corresponds to $t_{2g} \rightarrow \pi^*$ confirming the ability for the azopyridine ruthenium complexes to be used as photo sensitizer. Therefore, the δ -Cl isomers regarding each azopyridine ligand are admitted to be the best reactive ruthenium complexes. Besides, TDDFT prediction performed confirms the softness of δ -RuCl₂(Azpy)₂. However, δ -RuCl₂(Nazpy)₂ is admitted to be the most sensitive with a large band of absorption and an involvement of many molecular orbitals in electron transfer. On behalf of that investigation, the coming work will consist on applying δ -RuCl₂(Nazpy)₂ as photo-sensitizer over a well known active semi-conductor compound as TiO₂ anatase through dye-sensitized solar cell (DSSC) device.

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