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Study on molecular and electronic structures, and spectroscopic properties of azide ruthenium complexes with pyridine and β -picoline ligands

J.G. Małecki*, A. Maroń

Department of Crystallography, Institute of Chemistry, University of Silesia, 9th Szkolna St., 40-006 Katowice, Poland

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1. Introduction

In the chemistry of ruthenium, the coordination chemistry of complexes containing pyridine derivatives is one of the most frequently studied aspects. The wide interest is this field originates from the very rich redox chemistry and photophysics of these compounds. Even small changes in the coordination environment around the ruthenium atom plays a key role in altering the redox properties of its complexes, and thus complexation of ruthenium by various ligands is very interesting and widely studied [1–3]. These attributes of substituted pyridine-containing ruthenium compounds lead to their application in conversion of solar energy to electrical energy [4], in long-range electron transfer and energy translocation [5], molecular electronic devices [6], supramolecular self-assembly processes [7] and as DNA photoprobes [8,9]. The molecular and electronic structures of pyridine and picoline ruthenium(II) chloride and isothiocyanate complexes were studied earlier [10–12]. Additionally, thiocyanate ligands tune the spectral and redox properties of ruthenium(II) complexes by destabilizing the metal t_{2g} orbital. In general, azine ligands have energetically low π -antibonding orbitals, which can accept electrons from occupied metal *d* orbitals. As a consequence, they can exhibit charge transfer bands with interesting spectroscopic properties in the visible region.

ABSTRACT

The $[Ru(N_3)_2(PPh_3)(py)_3]$ and $[Ru(N_3)_2(PPh_3)_2(\beta-pic)_2]$ complexes have been prepared and studied by IR, NMR, UV–Vis spectroscopy and X-ray crystallography. The complexes were prepared in the reactions of $[RuCl_2(PPh_3)_3]$ with pyridine, β -picoline and NaN₃ in methanol solutions. The electronic structures of the obtained complexes have been calculated using the DFT/TD-DFT method. The *trans* effect of triphenylphosphine on the pyridine molecule has been studied using NBO and molecular orbital terms, and impact of the acceptor properties of the halide/pseudohalide co-ligands was indicated.

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Here, an experimental and quantum chemical study of ruthenium azide complexes with pyridine and β -picoline ligands is reported. The quantum chemical study includes characterization of the molecular and electronic structures of the complexes by analysis of their optimized molecular geometries, and their electronic populations using the natural bond orbitals scheme. The latter was used to identify the nature of the interactions between the ligands and the central ion. The calculated density of states showed the interactions and influences of the orbital composition on the frontier electronic structure. The time dependent density functional theory (TD-DFT) was finally used to calculate the electronic absorption spectra. Based on a molecular orbital scheme, these results allowed the interpretation of the UV–Vis spectra obtained at the experimental level.

2. Experimental

All reagents used in the synthesis of the complexes are commercially available and were used without further purification. The [RuCl₂(PPh₃)₃] complex was synthesised according to the literature method [13].

2.1. Synthesis of the complexes $[Ru(N_3)_2(PPh_3)(py)_3]$ (1) and $[Ru(N_3)_2(PPh_3)_2(\beta-pic)_2]$ (2)

The complexes were synthesised in the reaction between $[RuCl_2(PPh_3)_3]$ (0.2 g, 2×10^{-4} mol), NaN₃ (0.02 g) and pyridine



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or β -picoline (0.1 mL). A mixture of the compounds was refluxed in methanol (50 mL) for 3 h. After this time it was cooled and filtered. Crystals suitable for X-ray crystal analysis were obtained by slow evaporation of the reaction mixture.

Table 1

Crystal data and structure refinement details of the complexes $[Ru(N_3)_2(PPh_3)(py)_3]$ (1) and $[Ru(N_3)_2(PPh_3)_2(\beta-pic)_2]$ (2).

	1	2
Empirical formula	C33H30N9PRu	C48H44N8P2Ru
Formula weight	684.70	895.92
T (K)	295(2)	295(2)
Crystal system	monoclinic	triclinic
Space group	C2/c	ΡĪ
Unit cell dimensions		
a (Å)	34.498(6)	9.7160(8)
b (Å)	9.9413(5)	11.3665(8)
<i>c</i> (Å)	17.9742(8)	11.6723(11)
α (°)	90	103.932(7)
β (°)	96.815(10)	111.583(8)
γ (°)	90	103.946(7)
V (Å ³)	6120.7(11)	1083.1(2)
Ζ	8	1
Calculated density (mg/m ³)	1.486	1.374
Absorption coefficient (mm^{-1})	0.604	0.480
F(000)	2800	462
Crystal dimensions (mm)	$0.27 \times 0.10 \times 0.07$	$0.27 \times 0.10 \times 0.07$
θ range for data collection (°)	3.41-25.05	3.44-25.05
Index ranges	$-40\leqslant h\leqslant 40$	$-11 \leqslant h \leqslant 11$
	$-11 \leqslant k \leqslant 11$	$-13 \leqslant k \leqslant 13$
	$-20 \leqslant l \leqslant 21$	$-13 \leqslant l \leqslant 13$
Reflections collected	27352	13241
Independent reflections (R_{int})	5399 (0.0305)	3817 (0.0315)
Data/restraints/parameters	5399/0/397	3817/0/269
Goodness-of-fit (GOF) on F^2	1.014	1.058
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0291$	$R_1 = 0.0513$
	$wR_2 = 0.0635$	$wR_2 = 0.0971$
R indices (all data)	$R_1 = 0.0397$	$R_1 = 0.0686$
x . 1°CC	$WK_2 = 0.0659$	$WK_2 = 0.1015$
Largest difference in peak and hole $(a \ a^{-3})$	0.570 and -0.378	0.739 and -0.546

(e A⁻³)

[*Ru*(*N*₃)₂(*PPh*₃)(*py*)₃] (**1**): Yield 70%. IR (KBr, cm⁻¹): 3050 v_{ArH} ; 2039 $v_{(N=N=N)}$; 1635 v_{CN} , $v_{C=C}$; 1479 $\delta_{(C-CH in the plane)}$; 1432 v_{P-Ph} ; 1310 $v_{(N=N=N)}$; 1089 $\delta_{(C-CH in the plane)}$; 1027 $\delta_{(C-H out of the plane)}$; 748 $\delta_{(C-C out of the plane)}$; 696 $\delta_{(NNN)}$; 515 $v_{(P-Ph)}$. UV–Vis (methanol, nm), (log ε): 475.5 (1.31), 371.0 (2.04), 273.0 (sh), 211.0 (5.10). ¹H NMR (δ , CDCl₃): 8.621 (H_{Py}), 7.679 (H_{Py}), 7.700, 7.569–7.496 (m, PPh₃), 7.312 (H_{Py}). ³¹P NMR (δ , CDCl₃): 29.621 (s, PPh₃).

[$Ru(N_3)_2(PPh_3)_2(\beta$ - $pic)_2$] (2): Yield 68%. IR (KBr, cm⁻¹): 3059 v_{ArH} , 2920 v_{CH} ; 2040 $v_{(NNN)}$; 1639 v_{CN} , $v_{C=C}$; 1479 $\delta_{(C-CH \text{ in the plane})}$; 1329 $v_{(N=N=N)}$; 1434 v_{P-Ph} ; 1089 $\delta_{(C-CH \text{ in the plane})}$; 1028 $\delta_{(C-H \text{ out of the plane})}$; 790 $v_{Pic-ring}$, 750 $\delta_{(C-C \text{ out of the plane})}$; 698 $\delta_{(NNN)}$; 510 $v_{(P-Ph)}$. UV–Vis (methanol, nm), (log ε): 470.0 (1.09), 362.0 (3.38), 270.1 (sh), 213.0 (5.12). ¹H NMR (δ , CDCl₃): 8.398 (H_{Pic}), 7.684–7.469 (m, PPh₃), 7.539 (H_{Pic}), 7.212 (H_{Pic}), 2.344 (CH_{3(Pic)}). ³¹P NMR (δ , CDCl₃): 29.936 (s, PPh₃).

2.2. Physical measurements

Infrared spectra were recorded on a PerkinElmer FT-IR spectrophotometer in the spectral range of 4000–450 cm⁻¹ using KBr pellets. Electronic spectra were measured on a Lab Alliance UV–Vis 8500 spectrophotometer in the range of 600–180 nm in methanol solution. The ¹H and ³¹P NMR spectra were recorded at room temperature in CDCl₃ using a Bruker 400 spectrometer. Luminescence measurements were made in methanolic solutions on an F-2500 FL spectrophotometer at room temperature.

2.3. DFT calculations

The calculations were carried out using the GAUSSIAN09 [14] program. The DFT/B3LYP [15,16] method was used for the geometry optimization and electronic structure determination, and electronic spectra were calculated by the TD-DFT [17] method. The calculations were performed using the DZVP basis set [18] with *f* functions with exponents 1.94722036 and 0.748930908 on ruthenium atom, and polarization functions for all other atoms: 6-31g** – carbon, nitrogen and hydrogen. The PCM solvent model was used in the GAUSSIAN calculations with methanol as the solvent. The con-



Fig. 1. Experimental and calculated IR spectra of the [Ru(N₃)₂(PPh₃)(py)₃] complex.

tribution of a group to a molecular orbital was calculated using Mulliken population analysis. GaussSum 2.2 [19] was used to calculate group contributions to the molecular orbitals and to prepare the partial density of states (DOS) and overlap population density of states (OPDOS) spectra. The PDOS and OPDOS spectra were created by convoluting the molecular orbital information with caussian curves of unit height and FWHM of 0.3 eV.

2.4. Crystal structures determination and refinement

Red crystals of $[Ru(N_3)_2(PPh_3)(py)_3]$ (1) and $[Ru(N_3)_2(PPh_3)_2$ $(\beta-pic)_2$ (2) were mounted in turn on a Gemini A Ultra Oxford Diffraction automatic diffractometer equipped with a CCD detector, and used for data collection. X-ray intensity data were collected with graphite monochromated Mo K α radiation (λ = 0.71073 Å) at the temperature 295(2) K, with the ω scan mode. Ewald sphere reflections were collected up to $2\theta = 50.10^{\circ}$. The unit cell parameters were determined from least-squares refinement of the 11817 and 5907 strongest reflections for complexes 1 and 2, respectively. The details concerning crystal data and refinement are gathered in Table 1. Lorentz, polarization and empirical absorption correction using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm [20] were applied. The structures were solved by the Patterson method and subsequently completed by difference Fourier recycling. All the non-hydrogen atoms were refined anisotropically using the full-matrix, least-squares technique. The hydrogen atoms were treated as "riding" on their parent carbon atoms and assigned isotropic temperature factors equal to 1.2 times the value of the equivalent temperature factor of the parent atom. The OLEX2 [21] program was used for all the calculations. The atomic scattering factors used were those incorporated in the computer programs.

3. Results and discussion

The reactions of the [RuCl₂(PPh₃)₃] complex with an excess of pyridine. B-picoline and sodium azide have been carried out. Refluxing the starting ruthenium(II) complex with the ligands in methanol leads to two new complexes with formula $[Ru(N_3)_2(PPh_3)(py)_3]$ (1) and $[Ru(N_3)_2(PPh_3)_2(\beta-pic)_2]$ (2) in good yields. The IR spectra of the complexes show sharp and strong absorption bands at 2040 cm⁻¹ assignable to the asymmetric stretching frequency of the terminal azide groups. The symmetric N_3^- stretching frequency is observed at 1310 and 1329 cm⁻¹ for complexes (1) and (2), respectively. The characteristic bands of the C=C and C=N stretching modes of pyridine occur at 1635 and 1639 cm⁻¹ in complexes **1** and **2**, respectively. The experimental and calculated infrared spectra of complex **1** are presented in Fig. 1. The ³¹P{¹H} NMR spectra of the complexes present a singlet at 29.621 ppm for 1 and 29.936 ppm for 2. The singlet in the spectrum of complex 2 indicates a trans conformation of PPh₃ ligands in consistence with the crystallographic data. The ¹H NMR spectra of the complexes displayed sets of signals, reported in the experimental section, that are ascribed to the pyridine (β -picoline) and triphenylphosphine ligands.

The complexes **1** and **2** crystallize in the monoclinic C2/c and triclinic $P\overline{1}$ space groups, respectively, and their molecular structures are shown in Fig. 2. Selected bond lengths and angles are listed in Table 2. In the complexes, the ruthenium atoms have an octahedral environment, and the maximum distortion from an ideal octahedron is visible in complex **1** in the fact that the angle between the azide ligands is $175.18(8)^\circ$. The azide N=N bond lengths values fall in the range 1.151(3)-1.186(5)Å, similar to the values observed earlier for azide complexes [22–25]. The azido groups are slightly bent, with an angle near 176° . The Ru–N_(pv)

distances are normal and comparable with distances in other ruthenium complexes containing N-heterocyclic ligands. In the structure of complex **1**, the Ru(1)–N(8) distance is elongated by about 0.05 Å compared to the length of the other two ruthenium–pyridine bonds. This bond elongation is a result of the impact of the phosphine ligand in a *trans* position on the pyridine–N(8) molecule.

The conformations of the complex molecules are stabilized by intra- and intermolecular weak hydrogen bonds, details of which are collected in Table 3. Additionally, in the structure of complex **2**, some weak electronic interactions (π – π stacking) between the PPh₃ phenyl and picoline rings are possible. The plane-to-plane distance between the centroids, determined by C(7) to C(12) carbons and the picoline ring is equal to 3.731(3) Å, indicating a π – π stacking interaction. The angle between the normal to the phenyl and picoline planes is 18.4(3)°.



Fig. 2. Ortep drawings of the $[Ru(N_3)_2(PPh_3)(py)_3]$ and $[Ru(N_3)_2(PPh_3)_2(\beta-pic)_2]$ complexes with 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

3.1. Optimized geometries, hybrid and molecular orbitals description

The ground state geometries of the studied complexes were optimized in the singlet state using the DFT method with the B3LYP functional. The optimizations were carried out for gas phase molecules and in general the predicted bond lengths and angles are

Table 2

Selected bond lengths (Å) and angles (°) for the complexes $[Ru(N_3)_2(PPh_3)(py)_3]$ (1) and $[Ru(N_3)_2(PPh_3)_2(\beta-pic)_2]$ (2), with the optimized geometry values.

	1		2	
	Exp	Calc	Exp	Calc
Bond lengths (Å)				
Ru(1) - N(1)	2.108(2)	2.173	2.103(4)	2.168
Ru(1)-N(4)	2.119(2)	2.174	2.121(3)	2.172
Ru(1) - N(7)	2.1047(19)	2.144		
Ru(1)-N(8)	2.1681(19)	2.200		
Ru(1)-N(9)	2.1155(19)	2.169		
Ru(1)-P(1)	2.3137(6)	2.411	2.3952(12)	2.484
N(1)-N(2)	1.170(3)	1.207	1.186(5)	1.206
N(2)-N(3)	1.154(3)	1.165	1.157(6)	1.165
N(4)-N(5)	1.183(3)	1.207		
N(5)-N(6)	1.151(3)	1.165		
Angles (°)				
N(1)-Ru(1)-N(7)	89.31(8)	92.81		
N(7)-Ru(1)-N(9)	175.24(7)	175.36		
N(1)-Ru(1)-N(9)	89.94(8)	88.82		
N(7)-Ru(1)-N(4)	90.75(8)	90.22		
N(1)-Ru(1)-N(4)	175.18(8)	176.38	92.47(14)	93.35
N(9)-Ru(1)-N(4)	89.61(8)	90.22		
N(7)-Ru(1)-N(8)	87.85(7)	88.39		
N(1)-Ru(1)-N(8)	92.84(7)	90.22		
N(9)-Ru(1)-N(8)	87.50(7)	87.26		
N(4)-Ru(1)-N(8)	82.34(8)	87.93		
N(7)-Ru(1)-P(1)	94.03(6)	92.72		
N(1)-Ru(1)-P(1)	87.00(6)	87.92	90.22(11)	90.22
N(9)-Ru(1)-P(1)	90.63(5)	90.17		
N(4)-Ru(1)-P(1)	97.81(6)	92.72	89.16(10)	88.86
N(8)-Ru(1)-P(1)	178.12(5)	174.95		
N(1)-N(2)-N(3)	176.4(3)	177.76	176.4(5)	177.41
N(4)-N(5)-N(6)	176.2(3)	177.84		
Ru(1)-N(1)-N(2)	129.12(18)	124.28	132.9(3)	125.73
Ru(1)-N(4)-N(5)	134.24(18)	126.13		
Dihedral angles (°)				
P(1)-Ru(1)-N(1)-N(2)	-178.0(2)	131.8(5)	153.55	122.96
N(7)/N(4)-Ru(1)-N(1)-	87.9(2)	42.6(5)	61.07	34.09
N(8)/N(4A)-Ru(1)-N(1)-N(1)-N(2)	0.1(2)	-137.4(5)	-27.35	-145.91
$N(Q) = R_{11}(1) = N(1) = N(2)$	87 4(2)		11/ 50	
$P(1) = P_{11}(1) = P_{11}(1) = P_{11}(1)$	-07.4(2)		-114.39	
F(1) = Ku(1) = IN(4) = IN(5)	-/0.3(2)		-11/./5	
N(2) = KU(1) = N(4) = N(5)	$1/.\delta(2)$		-24.97	
N(0) = KU(1) = N(4) = N(5) N(0) = Ru(1) = N(4) = N(5)	105.0(2)		150 74	
IN(9) - KU(1) - IN(4) - IN(5)	-100.9(2)		130.74	

Table 3

Hydrogen bonds for $[Ru(N_3)_2(PPh_3)(py)_3]$ (1) and $[Ru(N_3)_2(PPh_3)_2(\beta-pic)_2]$ (2) (Å and °).

D−H···A	d(D-H)	$d(H \cdot \cdot \cdot A)$	$d(D \cdots A)$	∠(DHA)
1				
C(1)-H(1)N(5)	0.93	2.48	3.033(3)	118.4
C(5)-H(5)N(2)	0.93	2.60	3.326(3)	135.3
C(11)-H(11)N(1)	0.93	2.43	3.016(3)	121.2
C(15)-H(15)N(4)	0.93	2.35	2.974(3)	123.9
C(23)-H(23)N(4)	0.93	2.28	3.107(3)	147.8
2				
C(1)-H(1)N(1)	0.93	2.57	3.118(6)	118.1
C(1)-H(1)N(2)	0.93	2.51	3.117(6)	123.3
C(5)-H(5)N(1) #1	0.93	2.39	2.958(6)	119.5
C(14)-H(14)N(1)	0.93	2.52	3.056(6)	116.9

#1 −*x*, 1 − *y*, −*z*.

Table 4

Selected natural atomic charges and Ru-L bond order in the complexes 1 and 2.

	1	2
Natural atomic charges		
Ru	0.092	-0.193
N _(azide)	-0.487	-0.475
Р	1.259	1.244
N(8)/N(4)	-0.397	-0.387
N(7)	-0.407	
N(9)	-0.399	
Bond orders		
Ru–P	0.743	0.681
Ru-N _(azide)	0.543	0.547
Ru - N(7)/(4)	0.540	0.463
Ru-N(8)	0.477	
Ru–N(9)	0.457	

in agreement with the values based on the X-ray crystal structure data, and the general trends observed in the experimental data are reproduced well in the calculations. The calculated IR frequencies of complex **1**, shown in Fig. 1, confirm the accordance of the calculated structures with the experimental ones, and the differences between the calculated and experimental spectra mainly result from the negligence of intermolecular interactions for the gas phase. From the data collected in Table 2, one may see that the majority of differences between the experimental and calculated geometries are found in the Ru–P distance (~0.09 Å) and the maximum angle differences do not exceed 8.2°.

The NBO analyses were performed for the complexes which allowed the nature of the coordination between ruthenium and the atoms of the ligands directly interacting with it to be learned. This methodology also gave a better understanding of the optimized molecular structures. In the analysis, it was found that the N₃⁻ ligands exhibited covalent bonding with ruthenium. The calculated Wiberg bond indices have values close to 0.54 and the occupancies and hybridization are: 1.618_{BD} (0.219_{BD}^*) and $0.390(sp^{12.71}d^{11.59})_{Ru} + 0.921(sp^{9.54})_{N3}$ for complex **1**, and 1.620_{BD} (0.221_{BD}^*) and $0.397(sp^{13.43}d^{12.49})_{Ru} + 0.918(sp^{8.96})_{N3}$ for **2**. The data show that the Ru-N₃ bonds are polarized towards the azide ligands. The occupancy of the ruthenium azide bonds is below 2, suggesting redistributions of electron density in the molecules. The natural charges on the ruthenium central ions are close to zero (0.09 for 1 and -0.19 for 2) and the occupancies of the ruthenium d orbitals are as follows: **1** $d_{xy} - 1.77$; $d_{xz} - 1.90$; $d_{yz} - 1.89$; $d_{x^2-y^2} - 0.81$; $d_{z^2} - 0.74$ and **2** $d_{xy} - 1.42$; $d_{xz} - 1.46$; $d_{yz} - 1.41$; $d_{x^2-y^2}$ – 1.44; d_{z^2} – 1.57. Table 4 presents the atomic charges and Ru-L bond orders. The *d*-electron populations of 7.11 for 1 and 7.30 for 2 correspond to the oxidation state Ru(I), not to the formal oxidation state Ru(II). This is a supporting argument for ligand to d_{Ru} electron transfer. The data suggest that the donation from the ligands to d_{Ru} orbitals plays a role in the electronic structure of the complexes, and in order to determine the donation, the stabilization energies¹ were calculated. In these analyses, it has become evident that the pyridine ligands donate charge to ruthenium and the stabilization energies (ΔE_{ii}) are 251.22 (72.49) kcal/mol and 203.90 kcal/mol for complexes 1 and 2, respectively. The back donations from ruthenium to N-donor ligands in complexes 1 and 2 have values of 112.21 (34.17) and 75.84 kcal/mol, respectively. The values of the interactions between ruthenium and the pyridine molecule in the trans position to the PPh₃ ligand in complex **1** are reported in the

¹ ΔE_{ij} (kcal/mol) associated with delocalization is estimated by the second-order perturbative as: $\Delta E_{ij} = q_i (F(i,j)^2)/(\varepsilon_j - \varepsilon_i)$ where q_i is the donor orbital occupancy, ε_i , ε_j are diagonal elements (orbital energies) and F(i,j) is the off-diagonal NBO Fock or Kohn–Sham matrix element.

brackets. As one can see, the interactions are relatively weaker compared to the other Ru–py bond. The weakening of the interactions may also be seen in the Wiberg indices, which are decreased in comparison to the other ones (Ru–N(8) 0.424; Ru–N(7) 0.478; Ru–N(9) 0.457).

This effect may be associated with a strong σ -donor interaction of the phosphine with the ruthenium central ion and a relatively weak interaction of the pyridine acceptor. Accumulation of a partial charge on the $d_{x^2-v^2}$ orbital of ruthenium offsets the π -backdonation, and limits the σ -donation from pyridine. This *trans* influence is shown in Fig. 3. The overlap partial density of states diagram shows the weak acceptor properties of the pyridine ligand compared with the strong accepting possibility of the PPh₃ ligand. Additionally, one can see the weak interaction between the phosphine and pyridine ligands affected by the d_{Ru} orbital. A similar effect occurs in the chloride complex, however the elongation of the bond between ruthenium and pyridine in the *trans* position to the PPh₃ molecule is smaller (Ru-N_t 2.1527(14) Å) [11]. The differences in the strength of the trans effect in these complexes result from the donor-acceptor properties of the chloride and azide ligands. In Fig. 3, the OPDOS diagram showing the interaction between the ruthenium(II) central ion with the chloride and azide ligands is presented as the insert. Much stronger interaction properties of the chloride ligand allow a redistribution of the electron density from the b_1 term $(d_{x^2-y^2})$ of ruthenium and thus a stronger interaction with the pyridine donor in the trans position to the PPh₃ ligand.

In the studied complexes, the HOMO and HOMO-1 molecular orbitals are composed of d ruthenium and π_{azide} orbitals. HOMO-2 is localized on the ruthenium central ion in complex 1 and on the azide ligands in 2, as is shown in Fig. 4. The HOMO, H and LUMO, L abbreviations denote the Highest Occupied Molecular Orbital and Lowest Unoccupied Molecular Orbital. In the frontier virtual molecular orbitals, d_{Ru} has a share in LUMO+10 and LUMO+13 in complex 1 and LUMO+1, LUMO+12 in 2. In LUMO+13 and LUMO+12, in addition to the $d_{x^2-y^2}$ orbital of ruthenium, the azide, PPh₃ and pyridine or picoline orbitals are visible. Fig. 5 presents the partial density of states of the complexes, which is a more realistic description of the frontier orbitals than a simplified molecular diagram. As it may be seen, the lowest unoccupied molecular orbitals in complex 1 are localized on the pyridine ligands in contrast to complex 2, in which the picoline ligands do not play a significant role in the lower LUMO orbitals. This difference in the electronic structure of the



Fig. 3. The overlap partial density of states (OPDOS) diagram for the interaction between the ruthenium central ion and the ligands in complex **1**.

complexes causes the mapping, is reflected in their spectroscopic properties, in particular with regard to the ability of fluorescence.



 $\begin{array}{l} \mbox{Fig. 4. Simplified molecular orbital diagrams for the complexes $[Ru(N_3)_2(PPh_3)$ (py)_3] (1) and $[Ru(N_3)_2(PPh_3)_2(\beta-pic)_2]$ (2). $ \end{array}$



Fig. 5. The density of states (DOS) diagrams for the complexes $[Ru(N_3)_2(PPh_3)(py)_3]$ (1) and $[Ru(N_3)_2(PPh_3)_2(\beta-pic)_2]$ (2). Dotted line represents the chloride DOS from the $[RuCl_2(PPh_3)(py)_3]$ complex.

3.2. Absorption and emission electronic spectra

The UV–Vis spectra of the complexes are very similar and they present bands with maxima close to 470 and 370 nm which are assigned to ${}^{1}A_{1} \rightarrow {}^{1}T_{1}$ and ${}^{1}A_{1} \rightarrow {}^{1}T_{2}$ transitions based on the pseudo-octahedral geometry of the molecules. The shoulders at 270 nm and the intense bands with maxima at 211 and 213 nm are attributed to $\pi^{b}_{curv} \rightarrow 3d_{abceberg}$, $\pi \rightarrow \pi^{*}_{a}$ c and $\pi \rightarrow \pi^{*}_{a}$ v transitions.

uted to $\pi^b_{C6H6} \rightarrow 3d_{phosphorus}$, $\pi \rightarrow \pi^*_{C-C}$ and $\pi \rightarrow \pi^*_{C=N}$ transitions. The values of the ligand field parameter 10Dq, calculated on the basis of the positions and molar extinction coefficients of electronic bands for the complexes, are equal to 22560 and 22498 cm^{-1} for complexes **1** and **2**, respectively. The Racah parameter *B* is equal to 360 cm^{-1} for **1** and 433 cm^{-1} for **2**, and the nepheloauxetic parameter β_{55} is 0.50 and 0.60 for complexes (1) and (2), respectively. The Racah parameters *B* are lower than 500, suggesting that the first transition bands have $d \rightarrow d$ character with a Metal-Ligand Charge Transfer (MLCT) admixture. The absorption electronic spectra of the complexes are calculated with use of the TD-DFT method. In the energy range corresponding to the first bands transitions, $HOMO \rightarrow LUMO$ experimental (53%)HOMO \rightarrow L+1 (41%), H-1 \rightarrow L+1 (76%) for complex **1** and HOMO \rightarrow LUMO (99%), HOMO \rightarrow L+3 (96%) for **2** are calculated. As the frontier HOMO is localized on the *d* ruthenium orbitals with an admixture of πN_3^- and the LUMOs are localized on the pyridine or β -picoline ligands with a contribution of d_{Ru} , the MLCT transitions are associated with these. The second transitions with maxima near 370 nm have HOMO \rightarrow L+5/6/7 and HOMO \rightarrow L+12 (74%) character, therefore these bands have MLCT character. In the energy region corresponding to the shoulders at 270 nm, the MLCT and LMCT (Ligand to Metal Charge Transfer) transitions are calculated and the highest energy bands are assigned to LLCT (Ligand to Ligand Charge Transfer) transitions.

The emission characteristics of the complexes have been examined in methanol solutions (with a concentration of 5×10^{-4} mol/dm³) at room temperature. The excitations were executed at wavelengths corresponding to the maxima of the first electronic absorptions. Emission was observed only in the case of the pyridine complex **1**, which is associated with differences in the electronic structure of these complexes, particularly involving the ligands in the lowest unoccupied molecular orbitals, that is clearly visible in the DOS diagrams presented in Fig. 5. Therefore, an emission originating from the lowest energy metal to ligand charge transfer (MLCT) state, derived from the excitation involving a $d_{\pi} \rightarrow \pi^*_{iigand}$ transition, is observed. The structure of the luminescence spec-



Fig. 6. Methanolic solution fluorescence of $[{\rm Ru}(N_3)_2({\rm PPh}_3)(py)_3]$ (1) excited at 439 nm.

trum, showed in Fig. 6, suggests that more than one state is involved in the luminescence processes. The excitation at 439 nm results in an emission with a maximum at a wavelength of 505 nm, at the same time a shoulder at 493 nm and a weak band with maximum at 650 nm are observed.

4. Conclusions

In this paper, an experimental and theoretical study of ruthenium(II) azide complexes with pyridine and 3-methylpyridine ligands has been made. The crystal structure and IR, ¹H, ³¹P NMR and UV–Vis spectroscopic properties of the complexes were determined. Theoretical calculations were carried out to determine the electronic structures of these complexes. A molecular orbital description of the HOMOs and LUMOs showed that the complexes can present an intramolecular charge transfer of metal to ligand character. The differences in the frontier molecular orbitals of these complexes determine their fluorescent properties. The *trans* influence of the triphenylphosphine ligand, shown in the molecular structure of complex **1**, has been studied by NBO and molecular orbital terms. A significant impact of the acceptor properties of the halide/pseudohalide co-ligands on the strength of the *trans* effect induced by phosphine was indicated.

Appendix A. Supplementary data

CCDC 818252 and 818088 contain the supplementary crystallographic data for the complexes $[Ru(N_3)_2(PPh_3)(py)_3]$ and $[Ru(N_3)_2(PPh_3)_2(\beta-pic)_2]$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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