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Synthesis, crystal, molecular and electronic structures of hydride carbonyl ruthenium(II) complexes with pyridine and its derivative ligands

J.G. Małecki

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

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ABSTRACT

 $[RuHCl(CO)(PPh_3)_2(py)]$, $[RuHCl(CO)(PPh_3)_2(pyIm)]$ and $[RuCl(CO)(PPh_3)_2(pyoh)]$ -2CH₃OH complexes (where py = pyridine, pyIm = imidazo[1,2- α]pyridine, pyoh = 2-hydroxy-6-methylpyridine) have been prepared and studied by IR, NMR, UV–Vis spectroscopy and X-ray crystallography. Electronic structures and bonding of the complexes were defined on the basis of DFT method, and the pyridine derivative ligands were compared on the basis of their donor–acceptor properties. Values of the ligand field parameter 10Dq and Racah's parameters were estimated for the studied compounds, and the luminescence properties were determined.

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1. Introduction

Chemistry of ruthenium complexes with nitrogen-containing ligands has been attracting continuous attention due to their variety of structures, reactivities, and photophysical and photochemical properties [1–3]. The azine ligands have energetically low lying π -antibonding orbitals, which can accept electrons from filled metal *d* orbitals. In consequence, they can exhibit charge transfer bands with interesting spectroscopic properties in the visible region [4]. Ligands containing pyridine ring are wide studied and their π -donor properties are interesting. Its combination with other donor atoms should in principle afford complexes with tunable spectroscopic properties [5,6]. The hydride ligand – a powerful σ -donor – is found to be very efficient at compensating the electron deficiency at the metal central ion in complexes. The "trans effect" of H⁻ ligand and the interaction between CO and N-donor ligands in trans positions to one another are stabilizing factors which explain stability of these complexes [7].

Besides, luminescent metal complexes are a fascinating class of molecules that have found applications in many areas, among which luminescent Ru(II) bipyridyl compounds have been extensively studied. The ruthenium(II) metal to ligand charge transfer (MLCT) compounds are known to display long lived luminescence life times. They are also extremely photo stable. In particular, ruthenium polypyridyl complexes have been researched extensively for decades as photochemical molecular devices due to their excellent chemical stability, facial electron transfer, strong luminescence and emission and relatively long-lived excited states [8,9]. Among the studied hydride-carbonyl ruthenium(II) complexes with pyridine derivatives ligands, the simple [RuHCl(CO) (py)(PPh₃)₂] complex has not been described like the complexes with imidazo[1,2- α]pyridine and 2-hydroxy-6-methylpyridine ligands. DFT and TDDFT calculations were performed to establish the nature of orbitals involved in transition processes and to correlate the structural parameters with the spectroscopic properties of the complexes.

2. Experimental

All reagents used for the synthesis of the complex are commercially available and have been used without further purification. The [RuHCl(CO)(PPh₃)₃] complex was synthesized according to the literature method [10].

2.1. Syntheses of $[RuHCl(CO)(PPh_3)_2(L)]$ complexes L = pyridine (py), imidazo[1,2- α]pyridine (pyIm), 2-hydroxy-6-methylpyridine

The complex was synthesized in a reaction between [RuHCl (CO)(PPh₃)₃] (1 × 10⁻⁴ mol) and pyridine, imidazo[1,2- α]pyridine or 2-hydroxy-6-methylpyridine (1 × 10⁻⁴ mol) in methanol solution



E-mail address: gmalecki@us.edu.pl

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(50 cm⁻³). The mixture of the compounds was refluxed in methanol by 3 h. After this time, it was cooled and filtered. The crystals suitable for X-ray crystal analysis were obtained by slow evaporation of the reaction mixture.

Compound **1**: Yield 78%. *Anal.* Calc. for $C_{42}H_{36}CINOP_2Ru: C$, 65.58; H, 4.72; N, 1.82. Found: C, 66.04; H, 4.69; N, 1.85%. IR (KBr): 3053 v_{ArH} ; 1995 $v_{(Ru-H)}$; 1920 $v_{(CO)}$; 1600 $v_{(CN)}$; 1586 $v_{(C=C)}$; 1480, 1311 $\delta_{(C-CH}$ in the plane); 1432 $v_{Ph(P-Ph)}$; 1091 $\delta_{(C-CH}$ in the plane); 998 $\delta_{(C-H}$ out of the plane); 745 $\delta_{(C-C}$ out of the plane); 695 $\delta_{(C-C}$ in the plane); 520 $v_{(P-Ph+P-Ru)}$. UV–Vis (methanol; log ε): 370.1 (1.13), 330.8 (1.90), 270.4 (2.96), 211.5 (4.98). ¹H NMR (δ , CDCl₃): 7.720–7.124 (m, PPh₃, py), -13.491 (t, H_{Ru}). ³¹P NMR (δ , CDCl₃): 45.709 (s, PPh₃). Luminescence: exc = 370 nm, emission = 430 nm; exc = 331 nm, emission = 380 nm.

Compound **2**: Yield 83%. *Anal.* Calc. for $C_{44}H_{37}ClN_2OP_2Ru$: C, 65.39; H, 4.61; N, 3.47. Found: C, 65.24; H, 4.69; N, 3.49%. IR (KBr): 3050 v_{ArH} ; 2016 $v_{(Ru-H)}$; 1900 $v_{(CO)}$; 1635 $v_{(CN)}$; 1571 $v_{(C=C)}$; 1480, 1313 $\delta_{(C-CH \text{ in the plane})}$; 1433 $v_{Ph(P-Ph)}$; 1092 $\delta_{(C-CH \text{ in the plane})}$; 741 $\delta_{(C-C \text{ out of the plane})}$; 693 $\delta_{(C-CH \text{ in the plane})}$; 741 $\delta_{(C-C \text{ out of the plane})}$; 360.3 (1.23), 310.2 (2.90), 265.1 (3.86), 211.3 (5.02). ¹H NMR (δ , CDCl₃): 8.141 (s, 1H_{imidazole}), 7.574–7.176 (m, PPh₃, pyIm), -13.322 (t, H_{Ru}). ³¹P NMR (δ , CDCl₃): 45.376 (s, PPh₃). Luminescence: exc = 360 nm, emission = 420 nm; exc = 310 nm, emission = 370 nm.

Compound **3:** Yield 83%. *Anal.* Calc. for $C_{45}H_{44}ClNO_4P_2Ru: C$, 62.75; H, 5.15; N, 1.63. Found: C, 62.79; H, 5.23; N, 1.59%. IR (KBr): 3435 v_{OH} ; 3052 v_{ArH} ; 1940 $v_{(CO)}$; 1712 $v_{(CN)}$; 1601 $v_{(C=C)}$; 1471 $\delta_{(C-CH \text{ in the plane})}$; 1435 $v_{Ph(P-Ph)}$; 1092 δ_{OH} ; 1028 $\delta_{(C-H \text{ out of the plane})}$; 745 $\delta_{(C-C \text{ out of the plane})}$; 696 $\delta_{(C-C \text{ in the plane})}$; 522 $v_{(P-Ph+P-Ru)}$. UV–Vis (methanol; log ε): 368.8 (1.23), 291.6 (2.90), 261.0 (2.81), 216.4 (4.92). ¹H NMR (δ , CDCl₃): 7.283–6.857 (m, PPh₃, pyo), 2.508 (s, CH₃), 3.260, 2.618 (CH₃OH). ³¹P NMR (δ , CDCl₃): 45.681, 40.035 (d, PPh₃). Luminescence: exc = 360 nm, emission = 415 nm; exc = 292 nm, emission = 375 and 450 nm.

2.1.1. Physical measurements

Infrared spectra were recorded on a Nicolet Magna 560 spectrophotometer in the spectral range 4000–400 cm⁻¹ using KBr pellets. Electronic spectra were measured on a Lab Alliance UV–Vis 8500 spectrophotometer in the range of 500–180 nm in methanol solution. The ¹H and ³¹P NMR spectra were obtained at room temperature in CDCl₃ using Bruker 400 spectrometer. Luminescence measurements were made on a F-2500 FL spectrophotometer at room temperature. Elemental analyses (C, H, N) were performed on a Perkin–Elmer CHN-2400 analyzer.

2.1.2. DFT calculations

The calculations were carried out using GAUSSIAN09 [11] program. The DFT/B3LYP/CAM-B3LYP [12-14] method was used for the geometry optimization and electronic structure determination, and electronic spectra were calculated by TD-DFT [15] method. The calculations were performed using the DZVP basis set [16] with f functions with exponents 1.94722036 and 0.748930908 on ruthenium atom, and polarization functions for all other atoms: 6-31g** - sulfur, carbon, nitrogen and 6-31g - hydrogen. The PCM (Polarizable Continuum Model) solvent model was used in the GAUSSIAN calculations with methanol as the solvent. Natural bond orbital (NBO) calculations were performed with the NBO code [17] included in GAUSSIAN09. The contribution of a group to a molecular orbital was calculated using Mulliken population analysis. GAUSSSUM 2.2 [18] 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 DOS and OPDOS spectra were created by convoluting the molecular orbital information with GAUSSIAN curves of unit height and FWHM (Full Width at Half Maximum) of 0.3 eV. Mayer bond orders were calculated with use of OMFORGE program [19].

Table 1

Crystal data and structure refinement details of [RuHCl(CO)(py)(PPh_3)2] (1), [RuHCl(CO)(PPh_3)2(pyIm)] (2) and [RuCl(CO)(PPh_3)2(pyoh)]·2CH_3OH (3) complexes.

	1	2	3
Empirical formula	C42H36CINOP2Ru	C44H37CIN2OP2Ru	$C_{43}H_{36}CINO_2P_2Ru, 2(CH_4O)$
Formula weight	769.18	808.22	861.27
Т (К)	298.0(2)	295.0(2)	295.0(2)
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/c$	ΡĪ
Unit cell dimensions			
a (Å)	15.8866(12)	11.069(2)	11.277(2)
b (Å)	14.1353(8)	24.400(5)	11.535(3)
c (Å)	16.0535(15)	28.016(6)	18.133(5)
α (°)	90	90	76.19(2)
β (°)	97.903(7)	92.41(3)	88.818(12)
γ (°)	90	90	80.45(2)
V (Å ³)	3570.8(5)	7560(3)	2258.4(10)
Ζ	4	8	2
$D_{\text{Calc.}}$ (Mg/m ³)	1.431	1.420	1.267
Absorption coefficient (mm ⁻¹)	0.638	0.607	0.517
F(000)	1576	3312	888
Crystal dimensions (mm)	$0.17 \times 0.16 \times 0.07$	$0.22\times0.21\times0.06$	$0.34 \times 0.27 \times 0.14$
θ Range for data collection (°)	3.37-25.05	3.40-25.05	3.47-25.05
Index ranges	$-18 \leqslant h \leqslant 15$	$-13 \leqslant h \leqslant 10$	$-13 \leqslant h \leqslant 13$
	$-16 \leqslant k \leqslant 16$	$-23 \leqslant k \leqslant 28$	$-13 \leqslant k \leqslant 13$
	$-16 \leqslant l \leqslant 19$	$-33 \leqslant l \leqslant 25$	$-21 \leqslant l \leqslant 21$
Reflections collected	10 291	33 103	40 553
Independent reflections (<i>R</i> _{int})	6315 (0.0740)	13 342 (0.0298)	7972 (0.0342)
Data/restraints/parameters	6315/0/437	13 342/0/927	7972/0/490
Goodness-of-fit (GOF) on F ²	0.990	1.022	1.068
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0397$	$R_1 = 0.0381$	$R_1 = 0.0418$
	$wR_2 = 0.0714$	$wR_2 = 0.0800$	$wR_2 = 0.1224$
R indices (all data)	$R_1 = 0.0768$	$R_1 = 0.0600$	$R_1 = 0.0512$
	$wR_2 = 0.0819$	$wR_2 = 0.0844$	$wR_2 = 0.1285$
Largest difference in peak and hole ($e Å^{-3}$)	1.003 and -0.638	0.421 and -0.543	1.250 and -0.646



Fig. 1. ORTEP drawing of [RuHCl(CO)(py)(PPh₃)₂] (1), [RuHCl(CO)(PPh₃)₂(pyIm)] (2) and [RuCl(CO)(PPh₃)₂(pyoh)]·2CH₃OH (3) with 50% probability displacement ellipsoids. Hydrogen atoms (except Ru–H) and solvent molecules are omitted for clarity.

2.2. Crystal structures determination and refinement

Crystals of [RuHCl(CO)(py)(PPh₃)₂] (1), [RuHCl(CO)(PPh₃)₂ (pyIm)] (2) and $[RuCl(CO)(PPh_3)_2(pyoh)] \cdot 2CH_3OH$ (3) were mounted in turn on an Xcalibur, Atlas, Gemini 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 temperature 298.0(2) K (1) or 295.0(2) K (2), (3), with ω scan mode. Ewald sphere reflections were collected up to 2θ = 50.10. The unit cell parameters were determined from least-squares refinement of the setting angles of 4074, 14 943 and 25 105 strongest reflections for complexes 1, 2 and 3, respectively. Details concerning crystal data and refinement are gathered in Table 1. During the data reduction, the decay correction coefficient was taken into account. Lorentz, polarization, and numerical absorption corrections were applied. The structures were solved by Patterson method. All the non-hydrogen atoms were refined anisotropically using full-matrix, least-squares technique on F^2 . The Ru–H hydrogen atoms were found from difference Fourier synthesis after four cycles of anisotropic refinement, and refined as "riding" on the adjacent atom with individual isotropic temperature factor equal 1.2 times the value of equivalent temperature factor of the parent atom, with geometry idealization after each cycle. The OLEX2 [20] program was used for all the calculations. Atomic scattering factors were those incorporated in the computer programs.

3. Results and discussion

The [RuHCl(CO)(py)(PPh₃)₂], [RuHCl(CO)(PPh₃)₂(pyIm)] and [RuCl(CO)(PPh₃)₂(pyoh)] complexes were obtained by the reaction of [RuHCl(CO)(PPh₃)₃] with pyridine (py), imidazo[1,2- α]pyridine (pyIm) or 2-hydroxy-6-methylpyridine (pyoh) in methanol solutions. Elemental analyses of the complexes are in a good agreement with their formulas. The ¹H NMR spectra of the complexes

displayed sets of signals, given in experimental section, that where ascribed to N-heteroaromatic and triphenylphosphine ligands. The triplets at -13.491 and -13.322 ppm indicated the hydride ligand in complexes **1** and **2**, respectively. The singlets in ³¹P NMR spectra of the complexes at 45.709 and 45.376 ppm indicated both the triphenylphosphine ligands in the compounds are equivalent and they are mutually *trans* disposed. On the ³¹P NMR spectrum of complex **3** two doublets at 45.681, 40.035 ppm indicates the *cis* configuration of PPh₃ ligands.

In the IR spectrum of complex **1**, the ring C=N stretching modes of the pyridine ligands are present at 1600 cm⁻¹, 1635 cm⁻¹ for complex **2** and the imidazo[1,2- α]pyridine C=N and C=C stretches are found at 1635 and 1571 cm⁻¹. The intense bands around 1995 and 2016 cm⁻¹ in IR spectra indicate the presence of hydride ligands in the complexes **1** and **2**, respectively. The stretching modes of the carbonyl group are observed at 1920, 1900 and 1940 cm⁻¹ and the stretching modes of the C-H are observed at 3053, 3050 and 3052 cm⁻¹, for complexes **1**, **2** and **3**, respectively. The phenyl ring C-H bend mode is visible in the bands with maxima at 1480, 1432, 1311 cm⁻¹ in **1**, 1480, 1433, 1313 cm⁻¹ in **2** and 1471, 1435 and 1028 cm⁻¹ in complex **3**. The stretching frequency of the Ru–N bond is at 520 cm⁻¹ in complex **1**, 519 cm⁻¹ in **2** and 522 cm⁻¹ in **3**.

The complexes crystallize in the monoclinic space group $P2_1/n$ and $P2_1/c$, **1** and **2**, respectively and the complex **3** crystallizes in the triclinic \bar{P}_1 space group. The crystal structure of complex **2** is built up of two independent molecules in the asymmetric unit. Both molecules have the same conformation. The relative orientation of molecules is depicted in Fig. 1, which also shows molecular structure of complexes 1, 3 and the displacement ellipsoids of the non-hydrogen atoms. The selected bond lengths and angles are listed in Table 2. In the complexes, the ruthenium atom has a disordered octahedral environment. The longer Ru-H bond in the complexes 1 compared with 2 is in accordance with infra red spectral data. The triphenylphosphine ligands in complexes 1 and 2 are in *trans* positions and in complex 3 these ligands are mutually in *cis*. The disposition of PPh₃ ligands are in coincidence with ³¹P NMR data. In the structures of the complexes, weak hydrogen bonds [21,22] exist and these are collected in Table 3.

3.1. Electronic structure

To form an insight in the electronic structures and bonding properties of the studied complexes, the calculations in the DFT method were carried out. Before the calculations of electronic structures of the complexes, their geometries were optimized in singlet states using the DFT method with the B3LYP functional. 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–H(Ru) distance and the angle differences do not exceed 4°. The stabilization energies calculated in NBO analyses have shown that the lone pairs localized on the N(O)-donor atoms of ligands in the complexes donate the charge to ruthenium, and the stabilization energies (ΔE_{ii}) are 118.15, 46.17 and 147.58 kcal/mol for 1, 2 and 3, respectively. The back donations to pyridine type ligands are equal to 24.48, 21.24 and 33.62 kcal/mol for complexes 1, 2 and 3, respectively. The chloride ligands also donate charge to ruthenium central ions and the energies are equal to 52.52 and 37.04 kcal/mol (back donation 5.57 and 3.02 kcal/mol) for complexes 1 and 2, respectively. The data suggest that the donation from ligands to d_{Ru} orbitals plays a role in the electronic structure of the complexes which can be seen in the charges of ruthenium central ions. The natural atomic charges on the ruthenium central ion in the complexes are -0.90 in 1, -0.08 in 2 and -0.51 in complexes **3**.

In the HOMO orbitals of the complexes **1** and **2**, the *d* ruthenium orbitals contribute 51% in complex **1** and 48% in **2**, and the chloride ligands 40% and 43%, respectively. In the electronic structure of both complexes, d_{Ru} orbitals are diffused in the HOMO–1 to HOMO–7 energy range with participation between 10% and 43%. In the complex **3** HOMO orbital is composed from pyoh ligand (82%) and d_{Ru} orbitals (11%) and in the LUMO d_{Ru} orbitals play significant role with contribution of 27% (62% PPh₃). The orbitals HOMO–1, HOMO–2 and HOMO–3 of complex **3** are localized on the d_{Ru} and π_{Cl} orbitals. In the lower HOMO orbitals (HOMO–4 to HOMO–6) the ruthenium *d* orbitals play significant role with contribution of π orbitals of triphenylphosphine ligands. The LUMO orbitals of the complexes **1** and **2** are localized on the pyridine

Table 2

Selected bond lengths (Å) and angles (°) for [RuHCl(CO)(py)(PPh₃)₂] (1), [RuHCl(CO)(PPh₃)₂(pylm)] (2) and [RuCl(CO)(PPh₃)₂(pyoh)] (3) complexes.

1			2					3		
	Exp	Calc.		Exp		Exp	Calc.		Exp	Calc.
Bond lengths (Å)										
Ru(1)-C(1)	1.811(7)	1.855	Ru(1)-C(1)	1.799(3)	Ru(2)-C(44)	1.817(3)	1.856	Ru(1)-C(1)	1.817(4)	1.857
Ru(1) - N(1)	2.211(5)	2.276	Ru(1) - N(1)	2.161(2)	Ru(2)-N(3)	2.186(3)	2.250	Ru(1) - N(1)	2.090(3)	2.141
Ru(1) - P(1)	2.367(17)	2.436	Ru(1) - P(1)	2.346(9)	Ru(2)-P(3)	2.355(9)	2.430	Ru(1) - P(1)	2.344(10)	2.431
Ru(1) - P(2)	2.349(18)	2.429	Ru(1) - P(2)	2.334(9)	Ru(2) - P(4)	2.338(9)	2.429	Ru(1)-P(2)	2.362(11)	2.453
Ru(1)-Cl(1)	2.519(15)	2.596	Ru(1)-Cl(1)	2.542(10)	Ru(2)-Cl(2)	2.518(11)	2.594	Ru(1)-Cl(1)	2.417(10)	2.460
Ru-H1(Ru)	1.820(4)	1.610	Ru-H1(Ru)	1.510(2)	Ru(2)-H2A(Ru)	1.460(3)	1.600	Ru(1)-O(2)	2.184(2)	2.202
C(1) - O(1)	1.169(9)	1.165	C(1) - O(1)	1.159(4)	C(44) - O(2)	1.156(4)	1.165	C(1) - O(1)	1.161(4)	1.162
Angles (°)										
P(1)-Ru(1)-P(2)	176.77(6)	177.21	P(1)-Ru(1)-P(2)	176.45(3)	P(3)-Ru(2)-P(4)	176.93(3)	176.29	P(1)-Ru(1)-P(2)	100.44(4)	101.06
C(1)-Ru(1)-Cl(1)	98.34(19)	100.69	C(1)-Ru(1)-Cl(1)	105.10(10)	C(44) - Ru(2) - Cl(2)	102.60(10)	100.70	C(1)-Ru(1)-Cl(1)	94.98(12)	91.92
P(1)-Ru(1)-N(1)	89.49(14)	90.79	P(1)-Ru(1)-N(1)	89.12(6)	P(3)-Ru(2)-N(3)	90.77(6)	91.40	P(1)-Ru(1)-N(1)	89.07(7)	90.61
P(1)-Ru(1)-C(1)	91.10(2)	89.99	P(1)-Ru(1)-C(1)	90.76(10)	P(3)-Ru(2)-C(44)	89.24(9)	89.19	P(1)-Ru(1)-C(1)	94.60(11)	94.55
N(1)-Ru(1)-Cl(1)	91.03(13)	89.51	N(1)-Ru(1)-Cl(1)	87.29(7)	N(3)-Ru(2)-Cl(2)	84.92(8)	87.21	N(1)-Ru(1)-Cl(1)	81.77(8)	81.48
P(2)-Ru(1)-N(1)	91.06(14)	91.05	P(2)-Ru(1)-N(1)	91.50(6)	P(4)-Ru(2)-N(3)	89.87(6)	90.85	P(2)-Ru(1)-N(1)	163.98(7)	159.07
P(2)-Ru(1)-C(1)	87.90(2)	87.83	P(2)-Ru(1)-C(1)	87.89(10)	P(4)-Ru(2)-C(44)	89.74(9)	88.17	P(2)-Ru(1)-C(1)	89.88(12)	93.50
P(2)-Ru(1)-Cl(1)	94.02(6)	92.59	P(2)-Ru(1)-Cl(1)	94.26(3)	P(4)-Ru(2)-Cl(2)	95.66(3)	92.89	P(2)-Ru(1)-Cl(1)	86.87(4)	85.13
P(1)-Ru(1)-Cl(1)	89.16(6)	89.52	P(1)-Ru(1)-Cl(1)	89.25(3)	P(3)-Ru(2)-Cl(2)	87.38(3)	90.15	P(1)-Ru(1)-Cl(1)	167.95(3)	170.74
N(1)-Ru(1)-C(1)	170.60(2)	169.76	N(1)-Ru(1)-C(1)	167.60(12)	N(4)-Ru(2)-C(44)	172.46(12)	172.07	N(1)-Ru(1)-C(1)	102.28(14)	102.91
P(2)-Ru(1)-H(1)	90.4(15)	91.00	P(2)-Ru(1)-H(1)	85.6(9)	P(4)-Ru(2)-H(2A)	86.9(10)	87.00	P(2)-Ru(1)-O(2)	106.16(6)	102.33
Cl(1)-Ru(1)-H(1)	173.7(15)	174.00	Cl(1)-Ru(1)-H(1)	171.7(9)	Cl(2)-Ru(2)-H(2A)	170.6(11)	174.00	Cl(1)-Ru(1)-O(2)	85.07(7)	87.84
N(1)-Ru(1)-H(1)	84.4(15)	85.00	N(1)-Ru(1)-H(1)	84.4(9)	N(3)-Ru(2)-H(2A)	86.1(11)	86.00	N(1)-Ru(1)-O(2)	61.77(9)	61.31
C(1)-Ru(1)-H(1)	86.3(15)	85.00	C(1)-Ru(1)-H(1)	83.2(9)	C(44)-Ru(2)-H(2A)	86.4(11)	86.00	C(1)-Ru(1)-O(2)	163.92(13)	164.08
P(1)-Ru(1)-H(1)	86.50(15)	87.00	P(1)-Ru(1)-H(1)	90.9(9)	P(3)-Ru(2)-H(2A)	90.1(10)	90.00	P(1)-Ru(1)-O(2)	83.70(7)	84.12
Ru(1)-C(1)-O(1)	174.7(6)	175.49	Ru(1)-C(1)-O(1)	173.2(3)	Ru(2)-C(44)-O(2)	176.0(3)	176.59	Ru(1)-C(1)-O(1)	175.4(3)	174.97

Table 3 Hydrogen bonds for [RuHCl(CO)(py)(PPh₃)₂] (1), [RuH(Cl)(CO)(PPh₃)₂(pyIm)] (2) and [RuCl(CO)(PPh₃)₂(pyoh)]·2CH₃OH (3) complexes (Å and °).

D−H···A	<i>d</i> (D–H)	d(H···A)	$d(D \cdot \cdot \cdot A)$	<(DHA)
1				
$C(5)-H(5)\cdots Cl(1)$	0.93	2.66	3.332(7)	130.0
$C(11)-H(11)\cdots Cl(1)$	0.93	2.73	3.535(8)	145.5
$C(29)-H(29)\cdots Cl(1)$	0.93	2.75	3.403(9)	127.6
2				
$C(2)-H(2)\cdots Cl(1)$	0.93	2.71	3.245(4)	117.4
C(32)−H(32)···N(1)	0.93	2.82	3.427(4)	123.5
$C(45)-H(45)\cdots Cl(2)$	0.93	2.59	3.147(4)	118.7
$C(77)-H(77)\cdots Cl(2)$	0.93	2.46	3.332(4)	157.2
C(5)−H(5)···O(1) #1	0.93	2.49	3.385(5)	161.3
3				
C(25) - H(25) - O(2)	0.93	2.32	3.138(4)	146.0
C(31)−H(31)···O(2)	0.93	2.54	3.141(4)	123.0
C(98)–H(98C)···Cl(1) #2	0.96	2.79	3.732(13)	163.0

Symmetry transformations used to generate equivalent atoms: #1 - 1 + x, *y*, *z*; #2 1 - x, 1 - y, 2 - z.

(93%) or imidazo[1,2- α]pyridine ligands (97%). Virtual molecular orbitals with large contribution of d_{Ru} are LUMO+1 (12%, 15%, 13% for **1**, **2** and **3**, respectively), LUMO+2 (21%) in complex **3** and are diffused in energy scope corresponding to LUMO+14 to LUMO+17 (15–30% in **1**; 13–34% in **2**) in electronic structures of complexes **1** and **2**. In these unoccupied orbitals, the carbonyl ligand plays significant role with contributions 44–68% in complex

1 and 45–62% in 2. Fig. 2 shows the partial density-of-states (DOS) and overlap partial density-of-states (OPDOS) diagrams in terms of Mulliken population analysis, calculated using the GAUSSSUM program, for complexes 2 (the 1 and 2 complexes have similar electronic structures) and 3. The DOS plot mainly presents the composition of the fragment orbitals contributing to the molecular orbitals. As can be seen from the OPDOS plot, the chloride ligands have significant antibonding character in the HOMO and HOMO-1 molecular orbitals and bonding in lower occupied orbitals. The interactions of the carbonyl ligand with the Ru(II) d orbitals have positive values (bonding character) in the frontier HOMO orbitals and in lower occupied orbitals. In the occupied and virtual molecular orbitals, the values of the interaction between ruthenium and the pyridine or imidazo $[1,2-\alpha]$ pyridine ligand are comparable, indicating that these ligands have similar π -acceptor properties. This conclusion is confirmed by the proportion of the Ru(II) and N-heteroaromatic ligand in the frontier molecular orbitals. The 2hydroxy-6-methylpyridine ligand has stronger π -acceptor properties than pyridine or imidazo $[1,2-\alpha]$ pyridine as one can see from the OPDOS diagram for complex 3 presented in Fig. 2b. Furthermore, the Mayer bond orders for Ru-N(1) of 0.66 for complex 1, 0.69 for 2 and 0.92 for 3 show the weakness of this bond compared with the Ru-Cl (1.16, 1.26 and 1.80 in 1, 2 and 3, respectively) bond. The Ru-CO and Ru-H bonds orders also are much alike in the complexes with values equal to 2.7 and 1.7, respectively. The cis arrangement of the bulky PPh₃ ligands in the [RuCl(CO)(PPh₃)₂ (pyoh)] complex is probably connected with stronger π -accepting ability of phosphines in the cis arrangement than in the trans



Fig. 2. The density of states (DOS) and overlap partial density of states (OPDOS) diagrams for complexes 2 (a) and 3 (b).

one, and it has electronic origin. The Mayer orders for Ru–P bond for complexes **1** and **2** are close each other and have value of 1.40, and in complex **3** it is equal to 1.60. The ruthenium–phosphine backdonation leads to a decrease in the electron density on the metal atom, which in turn causes stronger σ ligand–metal donation. In this manner the ruthenium central ion is suitable accepting more charge from N,O-donor ligand as pyoh. Taking into account the stabilization energy analysis mentioned above, one can see that the 2-hydroxy-6-methylpyridine ligand is the strongest donor among studied ligands and it favours the *cis*-PPh₃ form over *trans*-PPh₃ one.

3.2. Electronic spectra

In the UV–Vis spectra of the complexes are similar and the maxima at 370, 331, 270 and 212 nm for complex **1**, 360, 310, 265, 211 for **2** and 368.8, 291.6, 261.0, 216.4 for **3** were measured. The assignments of the calculated transitions to the experimental bands are based on the criteria of energy and oscillator strength of the calculated transitions. In the description of the electronic transitions, only the main components of the molecular orbitals are taken into consideration. The electronic transitions were calculated by use the B3LYP functional and its long range corrected version CAM-B3LYP which using the Coulomb-attenuating method. As one can see from Fig. 3, the use of CAM-B3LYP functional provides better estimation of excitation energy especially for the transitions with *Charge-Transfer* character.

The first two experimental bands in the electronic spectra of the complexes are assigned to the transitions between the HOMO \rightarrow -LUMO+1 (69% for 1, 44% for 2, 64% for 3), HOMO \rightarrow LUMO (96% for 1, 69% for 2, 48% for 3) and HOMO-1 \rightarrow LUMO (93% for 1, 77% for 2, 57% for 3) molecular orbitals. As the HOMO, HOMO-1 and LUMO+1 are composed of the *d* ruthenium orbitals with admixture of π -chloride (1, 2) or π -PPh₃ (3), the transitions are of *Ligand Field* type (d \rightarrow d). The LUMOs are localised on the pyridine or imidazo[1,2- α]pyridine ligands, respectively in complexes 1 or 2 and *Metal-Ligand Charge Transfer* transitions are associated with these.

The bands observed at 270, 265 and 261 nm have been attributed to the *Metal–Ligand Charge Transfer* transitions $(d \rightarrow \pi^*_{PPh3/py/pyIm/Cl})$. In this energy region, the transitions between the HOMO \rightarrow LU-MO+4, HOMO–2 \rightarrow LUMO+3, HOMO–1 \rightarrow LUMO+5/6/7 were calculated. The highest energy bands with maxima at 212 nm and 211 nm are attributed to transitions of the *Ligand–Ligand Charge Transfer* type $(\pi \rightarrow \pi^*_{C=N})$.

Based on the pseudooctahedral geometry of the complexes and taking into account the d–d transitions assigned to ${}^{1}A_{1} \rightarrow {}^{1}T_{1}$ and ${}^{1}A_{1} \rightarrow {}^{1}T_{2}$ in octahedron, the ligand field parameter 10Dq can be estimated to 19 618 cm⁻¹ for the complex **1**, 22 417 cm⁻¹ for **2** and 25 604 cm⁻¹ for complex **3**. Adequately, Racah's parameters are B = 214, 299 and 479 cm⁻¹, C = 852, 1190 and 1906 cm⁻¹ and the nepheloauxetic parameter have values $\beta_{55} = 0.30$, 0.42 and 0.67 for complexes **1**, **2** and **3**, respectively.

The emission characteristics of the complexes have been examined in the methanol solutions (with concentration of 5×10^{-4} mol/dm³) at room temperature. The excitations were executed at two wavelengths corresponding to maxima of two first electronic absorptions, i.e., at 370, 331 nm for **1**, 360, 310 nm for **2** and 360, 292 nm for complex **3**. In all complexes, the emissions with maxima at 430, 420, 415 nm and 380, 370 and 375 nm (in the emission spectrum of complex **3** excited at 292 nm is visible lower intense band with maximum at 450 nm see Fig. 4) originating from the lowest energy metal to ligand charge transfer (MLCT) state, derived from the excitation involving a $d_{\pi} \rightarrow \pi_{\text{ligand}}$ transition are observed. The assignment is also supported by the analysis of the frontier orbitals of the corresponding complexes showing a contribution

of ligands nature. The excitations at shorter wavelengths gave stronger emission peaks. The emission of complex **2** is very intense compared to complexes **1** and **3** which is connected with the significant contribution of pyIm ligand in the frontier Homo and Lumo orbitals. In Fig. **4**, the luminescence spectra of the complexes **2** and **3** are presented, and in them (excited at 360 nm), a broadening and shoulders are visible. The complicated structure of the luminescence spectrum suggests that more than one state is involved in luminescence process. Hence the luminescence is of IL/MLCT origin in these systems. The singlet and triplet states of LF and LMCT type, which are close to the ground state energy can provide the radiationless deactivation channel for the complexes which explain relatively small intense of emission.

Summarizing, new ruthenium(II) complexes with N-heteroaromatic ligands have been synthesized. The molecular structures of the compounds are determined by X-ray, and the spectroscopic properties as infrared, ¹H, ³¹P NMR spectra were studied. Based on the crystal structures, the computational researches were made in order to determine the electronic structures of the complexes. The results were used to compare π -donor/acceptor properties of pyridine type ligands. The acceptor/donor properties of N(O)-donor ligands explained the differences in the triphenylphosphine ligands arrangement in the complexes. The ligands with strong donor properties favour the *cis*-PPh₃ form over *trans*-PPh₃ one in the



Fig. 3. The experimental and calculated (B3LYP and CAM-B3LYP functional) UV–Vis spectra of complexes 1 and 3.



Fig. 4. The emissions spectra of the complexes 2 and 3 in the methanolic solutions ($c = 5 \times 10^{-4} \text{ mol/dm}^3$).

complexes. This is connected with stronger π -accepting ability of phosphines in the cis arrangement [23].

On the basis of a pseudooctahedral configuration of the complexes and their electronic spectra, the values of the ligand field parameter 10Dq and Racah's parameters were estimated. Emission properties of the complexes have been examined. The emissions originating from the lowest energy metal to ligand charge transfer (MLCT) state, derived from the excitation involving a $d_{\pi} \rightarrow \pi_{\text{ligand}}$ transition are observed. The assignment is supported by the analysis of the frontier orbitals of the corresponding complexes showing a partial contribution of ligands nature.

Appendix A. Supplementary data

CCDC 769610, CCDC 782764 and CCDC 784018 contain the supplementary crystallographic data for [RuHCl(CO)(py)(PPh₃)₂], [RuHCl(CO)(PPh₃)₂(pyIm)] and [RuCl(CO)(PPh₃)₂(pyoh)]·2CH₃OH complexes, respectively. These data can be obtained free of charge from 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. Calculations have been carried out in Wroclaw Centre for Networking and Supercomputing (http:// www.wcss.wroc.pl).

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