Polyhedron 29 (2010) 1973-1979

Contents lists available at ScienceDirect

## Polyhedron

journal homepage: www.elsevier.com/locate/poly

# Synthesis, crystal, molecular and electronic structures of thiocyanate ruthenium complexes with pyridine and its derivatives as ligands

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#### ARTICLE INFO

Article history: Received 17 February 2010 Accepted 12 March 2010 Available online 27 March 2010

Keywords: Ruthenium thiocyanate complexes Pyridine γ-Picoline 2-(Aminomethyl)pyridine 2-(Hydroxymethyl)pyridine X-ray structure UV–Vis DFT TD-DFT

#### ABSTRACT

The complexes  $[Ru(SCN)_2(PPh_3)_2(L)_2]$ , where L = py and  $\gamma$ -pic, and  $[Ru(SCN)_2(PPh_3)_2(L)]$ , where L = py-2-CH<sub>2</sub>NH<sub>2</sub> and py-2-CH<sub>2</sub>O, have been prepared and studied by IR, NMR, EPR, UV–Vis spectroscopy and X-ray crystallography. The complexes were prepared in the reactions of  $[RuCl_2(PPh_3)_3]$  with pyridine,  $\gamma$ -picoline, 2-(aminomethyl)pyridine and 2-(hydroxymethyl)pyridine in methanol solutions. The electronic structures of the obtained compounds have been calculated using the DFT/TD-DFT method.

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#### 1. Introduction

In the chemistry of ruthenium, the coordination chemistry of complexes containing pyridine derivatives is one of the most studied aspects. The wide interest is this field originates from very rich redox chemistry and photophysics of these compounds. Even small changes in the coordination environment around ruthenium plays a key role in altering the redox properties of its complexes and thus complexation of ruthenium by different ligands is very interesting and widely studied [1–3]. These attributes of substituted pyridine containing ruthenium compounds leads to their application in the 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 [7,8] and as DNA photoprobes [9]. The molecular and electronic structure of pyridine and picoline ruthenium(II) chloride complexes were studied earlier [10,11]. Additionally, thiocyanate ligands tune the spectral and redox properties of ruthenium(II) complexes by destabilizing the metal t<sub>2g</sub> orbital. For example, the *cis* form of the [Ru<sup>(II)</sup>(4,4'-dicarboxy-2,2'-bipyridine)<sub>2</sub>(NCS)<sub>2</sub>] complex is one of the most efficient heterogeneous charge transfer sensitizers known to date and it is widely used in the nanocrystalline TiO<sub>2</sub> solar cell [12].

This paper presents the synthesis, crystal, molecular and electronic structures, and the spectroscopic characterization of some new thiocyanate ruthenium(II)/(III) complexes with pyridine type ligands.

#### 2. Experimental

All reagents used for the synthesis of the complexes are commercially available and were used without further purification. The [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] complex was synthesised according to the literature method [13].

#### 2.1. Synthesis of [Ru(SCN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(L)<sub>2</sub>]

The complexes were synthesized by the reaction between  $[RuCl_2(PPh_3)_3]$  (0.2 g;  $2 \times 10^{-4}$  mol), NH<sub>4</sub>SCN (0.03 g;  $4 \times 10^{-4}$  mol) and pyridine,  $\gamma$ -picoline, 2-(aminomethyl)pyridine or 2-(hydroxymethyl)pyridine ( $2.1 \times 10^{-4}$  mol). The reaction mixture was refluxed in methanol ( $50 \text{ cm}^{-3}$ ) for 2 h. After this time, it was cooled and filtered, and crystals suitable for X-ray crystal analysis were obtained by slow evaporation of the reaction mixture.

#### 2.2. [Ru(SCN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(py)<sub>2</sub>] (1)

Yield 72%. IR (KBr): 3050  $v_{CH}$ ; 2090  $v_{(CN \text{ from SCN})}$ ; 1601  $v_{CN}$ ,  $v_{C=C}$ ; 1480, 1309  $\delta_{(C-CH \text{ in the plane})}$ ; 1432  $v_{P-Ph}$ ; 1088  $\delta_{(C-CH \text{ in the plane})}$ ;



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<sup>0277-5387/\$ -</sup> see front matter  $\circledcirc$  2010 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2010.03.015

1011  $\delta_{(C-H \text{ out of the plane})}$ ; 867  $\nu_{(SC \text{ from SCN})}$ ; 741  $\delta_{(C-C \text{ out of the plane})}$ ; 692  $\delta_{(C-C \text{ in the plane})}$ ; 524  $\nu_{(P-Ph+P-Ru)}$ ; 504  $\delta_{(CNS)}$ . UV–Vis (methanol; log  $\varepsilon$ ); nm: 435.1 (2.91), 347.5 (3.90), 238.8 (4.86), 208.4 (5.12). <sup>1</sup>H NMR ( $\delta$ , DMSO  $d_6$ ): 8.433 (d, H<sub>Py</sub>), 7.913 (d, H<sub>Py</sub>), 7.637–7.129 (m, PPh<sub>3</sub>), 7.392 (d, H<sub>Py</sub>). <sup>31</sup>P NMR ( $\delta$ , CDCl<sub>3</sub>): 45.545 (s, PPh<sub>3</sub>), 39.853 (s, PPh<sub>3</sub>).

#### 2.3. [Ru(SCN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(γ-pic)<sub>2</sub>]·CH<sub>3</sub>OH (**2**)

Yield 78%. IR (KBr): 3345  $v_{OH}$ ; 3051  $v_{ArH}$ ; 2917  $v_{CH}$ ; 2100  $v_{(CN from SCN)}$ ; 1619  $v_{CN}$ ,  $v_{C=C}$ ; 1480, 1313  $\delta_{(C-CH in the plane)}$ ; 1432  $v_{P-Ph}$ ; 1090  $\delta_{(C-CH in the plane)}$ ; 1025  $\delta_{(C-H out of the plane)}$ ; 851  $v_{(SC from SCN)}$ ; 808  $v_{Pic-ring}$ ; 743  $\delta_{(C-C out of the plane)}$ ; 696  $\delta_{(C-C in the plane)}$ ; 524  $v_{(P-Ph+P-Ru)}$ ; 494  $\delta_{(CNS)}$ . UV–Vis (methanol; log  $\varepsilon$ ); nm: 405.7 (2.99), 314.1 (3.38), 222.6 (4.86), 212.6 (5.12). <sup>1</sup>H NMR ( $\delta$ , DMSO  $d_6$ ): 8.616 (d, H<sub>Pic</sub>), 7.637–7.129 (m, PPh<sub>3</sub>), 7.390 (d, H<sub>Pic</sub>), 2.507 (d, CH<sub>3(Pic)</sub>), 4.095 (OH<sub>(MeOH)</sub>), 3.346 (CH<sub>3(MeOH)</sub>). <sup>31</sup>P NMR ( $\delta$ , CDCl<sub>3</sub>): 45.664 (s, PPh<sub>3</sub>), 39.986 (s, PPh<sub>3</sub>).

#### 2.4. [Ru(SCN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(py-2-CH<sub>2</sub>NH<sub>2</sub>)] (3)

Yield 67%. IR (KBr): 3413  $v_{NH2}$ ; 3240  $v_{ArH}$ ; 3055, 2916  $v_{CH}$ ; 2106, 2074  $v_{(CN from SCN)}$ ; 1608  $v_{CN}$ ,  $v_{C=C}$ ; 1480, 1276  $\delta_{(C-CH in the plane)}$ ; 1434  $v_{P-Ph}$ ; 1092  $\delta_{(C-CH in the plane)}$ ; 964  $\delta_{(C-H out of the plane)}$ ; 878  $v_{(SC from SCN)}$ ; 750  $\delta_{(C-C out of the plane)}$ ; 699  $\delta_{(C-C in the plane)}$ ; 525  $v_{(P-Ph+P-Ru)}$ ; 511  $\delta_{(CNS)}$ . UV–Vis (methanol; log  $\varepsilon$ ); nm: 402.4 (1.89), 312.5 (2.71), 253.6 (4.05) sh, 208.7 (4.84). <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>): 8.253 (s, H), 7.757 (m, Py-2-CH<sub>2</sub>NH<sub>2</sub>) 7.400–7.104 (m, PPh<sub>3</sub>), 4.414 (NH), 1.582 (CH<sub>2</sub>). <sup>31</sup>P NMR ( $\delta$ , CDCl<sub>3</sub>): 45.276 (d, PPh<sub>3</sub>); 42.153 (d, PPh<sub>3</sub>)<sup>2</sup>J<sub>AB</sub> = 32.19 Hz.

#### 2.5. [Ru(SCN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(py-2-CH<sub>2</sub>O)]·CH<sub>3</sub>OH (4)

Yield 64%. IR (KBr): 3347  $v_{OH}$ ; 3055  $v_{ArH}$ ; 2939  $v_{CH}$ ; 2106  $v_{(CN from SCN)}$ ; 1606  $v_{CN}$ ,  $v_{C=C}$ ; 1480, 1315  $\delta_{(C-CH in the plane)}$ ; 1433  $v_{P-Ph}$ ; 1091  $\delta_{(C-CH in the plane)}$ ; 952  $\delta_{(C-H out of the plane)}$ ; 844  $v_{(SC from SCN)}$ ; 743  $\delta_{(C-C out of the plane)}$ ; 697  $\delta_{(C-C in the plane)}$ ; 523  $v_{(P-Ph+P-Ru)}$ ; 513  $\delta_{(CNS)}$ . UV–Vis (methanol; log  $\varepsilon$ ); nm: 510.6 (2.72), 329.2 (2.35), 276.6 (3.14), 215.0 (4.27). <sup>31</sup>P NMR ( $\delta$ , CDCl<sub>3</sub>): 55.572 (d, PPh<sub>3</sub>); 41.640 (d, PPh<sub>3</sub>) <sup>2</sup>J<sub>AB</sub> = 36.65 Hz.

#### 2.6. Physical measurements

Infrared spectra were recorded on a Nicolet Magna 560 spectrophotometer in the spectral range 4000–400 cm<sup>1</sup> with the sample in the form of a KBr pellet. Electronic spectra were measured on a Lab Alliance UV–Vis 8500 spectrophotometer in the range 700–180 nm in acetonitrile solution. The <sup>1</sup>H and <sup>31</sup>P NMR spectra were obtained at room temperature in CDCl<sub>3</sub> using a Bruker 400 spectrometer. EPR spectra were recorded as powder samples at 298 K on a Bruker EMX-10 spectrometer using 100 kHz field modulation.

#### 2.7. 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 of 1.94722036 and 0.748930908 on the ruthenium atom, and polarization functions for all other atoms: 6-31 g(2d,p) – sulfur, 6-31 g<sup>\*\*</sup> – carbon, nitrogen and 6-31 g(d,p) – hydrogen. The PCM solvent model was used in the Gaussian calculations with methanol as the solvent. The contribution 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 Gaussian curves of unit height and FWHM of 0.3 eV.

#### 2.8. Crystal structure determination and refinement

Yellow crystals of [Ru(SCN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(py)<sub>2</sub>] (1), [Ru(SCN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>- $(\gamma - pic)_2$ ]·CH<sub>3</sub>OH (2), [Ru(SCN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(py-2-CH<sub>2</sub>NH<sub>2</sub>)] (3) and [Ru(SCN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(py-2-CH<sub>2</sub>O)]·CH<sub>3</sub>OH (**4**) were mounted in turn on a Xcalibur, Atlas, Gemini ultra Oxford Diffraction automatic diffractometer equipped with a CCD detector, and were used for data collection. X-ray intensity data were collected with graphite monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) at a temperature of 295.0(2) K, with the  $\omega$  scan mode. Ewald sphere reflections were collected up to  $2\theta$  = 50.10. The unit cell parameters were determined from least-squares refinement of the setting angles of 25 967, 64 443, 14 984 and 11 713 strongest reflections for complexes 1, 2, 3 and 4, 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 direct methods. All the non-hydrogen atoms were refined anisotropically using the full-matrix, least-squares technique on  $F^2$ . All the hydrogen atoms were found from difference Fourier synthesis after four cycles of anisotropic refinement, and were refined as "riding" on the adjacent atom with individual isotropic temperature factors equal to 1.2 times the value of the 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 reactions of the  $[RuCl_2(PPh_3)_3]$  complex with pyridine,  $\gamma$ -picoline, 2-(aminomethyl)pyridine or 2-(hydroxymethyl)pyridine and ammonium thiocyanate have been performed. Refluxing the starting ruthenium(II) complex with the ligands in methanol leads to the complexes  $[Ru(SCN)_2(PPh_3)_2(L)_2]$ , where L = py and  $\gamma$ -pic, and  $[Ru(SCN)_2(PPh_3)_2(L)]$ , where  $L = py-2-CH_2NH_2$  and py-2-CH<sub>2</sub>O, with good yields. Infrared spectra of the obtained complexes have characteristic bands due to ligands vibrations. The  $v_{C=N}$  bands of the *N*-heteroaromatic ligands appear around 1601 cm<sup>-1</sup> for **1**, 1619 cm<sup>-1</sup> for **2**, 1608 cm<sup>-1</sup> for **3** and 1606 cm<sup>-1</sup> for **4**. The  $v_{CN}$  frequencies of the thiocyanate ligands have maxima close to 2100 cm<sup>-1</sup> which is characteristic of S-bonded complexes, but the electronic and steric effects caused by the N-donor ligands affects the  $v_{CN}$  frequency. The  $v_{CS}$  and  $\delta_{(CNS)}$  frequencies are observed at 867, 851, 878, 844 cm<sup>-1</sup> and 504, 494, 511, 513 cm<sup>-1</sup> for complexes 1, 2, 3 and 4, respectively. Because of the *trans* symmetry of the two NCS ligands in the complexes **1**, **2** and **4**, only one  $v_{CN}$ stretch is visible in the IR spectra, but the bands are broadened due to the not perfect *trans* disposition of the thiocyanate ligands. In the IR spectrum of complex 3, a band with a maximum at 2074 cm<sup>-1</sup> is visible, which is assigned to a  $v_{CN}$  stretch and indicates the mutually orientation of the SCN ligands is cis. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of the studied complexes **1** and **2** present two singlets, and in the spectra of complexes **3** and **4** two doublets, which are close to each other, are consistent with the structure confirmed by the X-ray analysis and indicate that the cis conformation of the PPh<sub>3</sub> ligands is kept upon coordination. The less shielded phosphorus atom in the complex **3** is probably positioned trans to the thiocyanate group due to the electron-withdrawing

#### Table 1

	1	2	3	4
Empirical formula	$C_{48}H_{40}N_4P_2RuS_2$	C <sub>51</sub> H <sub>48</sub> N <sub>4</sub> OP <sub>2</sub> RuS <sub>2</sub>	$C_{44}H_{38}N_4P_2RuS_2$	$C_{45}H_{40}N_3O_2P_2RuS_2$
Formula weight	899.97	960.08	849.93	881.93
Temperature (K)	295.0(2)	295.0(2)	295.0(2)	295.0(2)
Crystal system	monoclinic	trigonal	orthorhombic	orthorhombic
Space group	P21/c	R-3	$P2_{1}2_{1}2_{1}$	Pca21
Unit cell dimensions				
a (Å)	19.8773(4)	35.155(5)	13.4304(2)	17.6898(3)
b (Å)	10.92370(17)	35.155(5)	15.2689(2)	12.06743(19)
<i>c</i> (Å)	21.6045(5)	24.440(5)	19.5698(3)	19.4637(4)
α	90	90	90	90
β	114.142(3)	90	90	90
γ	90	120	90	90
Volume (Å <sup>3</sup> )	4280.78(14)	26158(8)	4013.12(10)	4154.92(13)
Ζ	4	18	4	4
$D_{\text{calc}}$ (Mg/m <sup>3</sup> )	1.396	1.096	1.407	1.410
Absorption coefficient $(mm^{-1})$	0.577	0.430	0.611	0.596
F (0 0 0)	1848	8928	1744	1812
Crystal dimensions (mm)	$0.39 \times 0.28 \times 0.16$	$0.38 \times 0.14 \times 0.11$	$0.33 \times 0.29 \times 0.20$	$0.17 \times 0.14 \times 0.13$
$\theta$ Range for data collection (°)	3.53-25.05	3.78-25.05	3.47-25.05	3.37-25.05
Index ranges	$-23 \leqslant h \leqslant 23$	$-41\leqslant h\leqslant 41$	$-15 \leqslant h \leqslant 16$	$-17 \leqslant h \leqslant 21$
	$-13 \leqslant k \leqslant 13$	$-41\leqslant k\leqslant 41$	$-18\leqslant k\leqslant 18$	$-14 \leqslant k \leqslant 12$
	$-25 \leqslant l \leqslant 25$	$-29 \leqslant l \leqslant 29$	$-22 \leqslant l \leqslant 23$	$-23 \leqslant l \leqslant 23$
Reflections collected	40118	30841	21245	20562
Independent reflections	7498 $[R(_{int}) = 0.0329]$	$10098[R(_{int}) = 0.0359]$	$6813 [R(_{int}) = 0.0241]$	7057 $[R(_{int}) = 0.0304]$
Data/restraints/parameters	7498/0/514	10 098/0/594	6813/0/489	7057/1/498
Goodness-of-fit (GOF) on F <sup>2</sup>	1.028	1.655	0.972	1.084
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0287$	$R_1 = 0.0512$	$R_1 = 0.0305$	$R_1 = 0.0296$
	$wR_2 = 0.0666$	$wR_2 = 0.1440$	$wR_2 = 0.0709$	$wR_2 = 0.0592$
R indices (all data)	$R_1 = 0.0415$	$R_1 = 0.0694$	$R_1 = 0.0390$	$R_1 = 0.0421$
	$wR_2 = 0.0704$	$wR_2 = 0.1584$	$wR_2 = 0.0730$	$wR_2 = 0.0612$
Largest difference in peak and hole ( $e Å^{-3}$ )	0.394 and -0.332	1.782 and -1.796	0.845 and -0.498	0.547 and -0.447

effect of the NCS ligand (in **4** it is in a *trans* position to an O donor). The <sup>1</sup>H NMR spectra of the complexes displayed sets of signals, given in experimental section, that are ascribed to *N*-heteroaromatic and triphenylphosphine ligands.

The EPR spectrum of a powder sample of complex **4** at room temperature at X-band frequencies revealed the absence of any hyperfine splitting due to interactions with any other nuclei present in the complex. In the spectrum two lines are visible with two different *g* values ( $g_x = g_y = 2.41$ ;  $g_z = 2.10$ ), indicative of magnetic anisotropy and suggestive of a tetragonal distortion in the octahedral geometry.

#### 3.1. Crystal structure

The  $[Ru(SCN)_2(PPh_3)_2(py)_2]$  and  $[Ru(SCN)_2(PPh_3)_2(\gamma-pic)_2]$ .  $CH_3OH$  complexes crystallise in the monoclinic  $P2_1/c$  and trigonal R-3 space groups, respectively. The complexes with the bidendate ligands 2-(aminomethyl)pyridine and 2-(hydroxymethyl)pyridine crystallise in the orthorhombic groups  $P2_12_12_1$  and Pca21. The molecular structures of the compounds are shown in Figs. 1-4. Selected bond lengths and angles are listed in Table 2. In all the studied complexes, the triphenylphosphine ligands are in *cis* positions and the pyridine and 4-methylpyridine ligands in complexes 1 and 2 have the same mutual orientation. In the complexes, the ruthenium atoms have an octahedral environment and the maximum distortion from octahedral is visible in complex 4 where the angle between the thiocyanate ligands is 171.19(11). The C-N and C-S bond lengths values fall in the 1.155(3)-1.156(3), 1.171(12)-1.174(13), 1.089(9)–1.144(6) and 1.146(4)–1.147(4) Å ranges for compounds 1-4, similar to those observed for thiocyanate complexes. These lengths are contrary to those expected for  $C \equiv N$ and C-S bonds, due to the contribution of two resonance structures: linear (M-\*N=C-S<sup>-</sup>) and bent  $\binom{N=C=S}{M}$  for thiocyanate metal complexes. The Ru–N and Ru–P distances are normal



**Fig. 1.** ORTEP drawing of [Ru(SCN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(py)<sub>2</sub>] with 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

and are comparable with the distances in other ruthenium complexes containing these heterocyclic ligands. The Ru–N–C mean angles are 177.25(9), 176.0(10), 174.8(7) and 175.4(3)° for complexes **1–4**, close to the higher value of the range observed [21] for metal-thiocyanate angles (130–180°) in structures containing the thiocyanate ion bonded to a metal through its nitrogen atom. The conformations of the studied compounds are stabilized by



**Fig. 2.** ORTEP drawing of  $[Ru(SCN)_2(PPh_3)_2(\gamma-pic)_2]$ ·CH<sub>3</sub>OH with 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.



Fig. 3. ORTEP drawing of  $[Ru(SCN)_2(PPh_3)_2(py-2-CH_2NH_2)]$  with 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

intra- and intermolecular weak hydrogen bonds, the data of which are collected in Table 3.

#### 3.2. Optimized geometries

The geometries of the studied complexes were optimized in singlet states using the DFT method with the B3LYP functional. The optimized geometric parameters are gathered in Table 2. In gen-



**Fig. 4.** ORTEP drawing of [Ru(SCN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(py-2-CH<sub>2</sub>O)]·CH<sub>3</sub>OH with 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

eral, the predicted bond lengths and angles are in a good agreement with the values based on the X-ray crystal structure data, and the general trends observed in the experimental data are well reproduced in the calculations.

The main differences between the optimized and experimental geometries of the studied compounds are visible in the Ru(1)–P(2) distance (~0.096 Å) for complex **1**, N(2)–C(2) ~0.095 Å for **3** and in the angles Ru(1)–N(1)–C(1) – 3.8° for **1**, N(1)–Ru(1)–N(2) – 3.5° for **3** and 6.1° Ru(1)–N(2)–C(2) for **4**.

#### 3.3. Electronic structure and NBO analysis

In the studied complexes, the HOMO and HOMO-1 molecular orbitals are composed of the *d* ruthenium and  $\pi_{SCN}$  orbitals with participation of 34, 35, 27% and 23% *d*<sub>Ru</sub> (HOMO) and 64, 62, 69, 76%  $\pi_{SCN}$  in complexes **1**, **2**, **3** and **4**, respectively. The LUMO and LUMO+1 orbitals in compounds 1, 2 and 3 are localized on the Ndonor ligands (above 90%), and in complex 4 on the py-2-CH<sub>2</sub>O (36%) and PPh<sub>3</sub> (37%) ligands with a contribution of  $d_{Ru}$  (27%). The ruthenium d orbitals play a significant role in the HOMO-4, HOMO-5 and HOMO-6 molecular orbitals of the studied compounds and LUMO+2 (29, 20%), LUMO+16 (16, 27%) and LUMO+17 (46, 50%) in complexes with monodendate N-heteroaromatic ligands. In the virtual molecular orbitals of complex 3 large contribution of  $d_{Ru}$  is visible in LUMO+13 (41%) and LUMO+14 (34%). In the case of the ruthenium(III) complex 4 LUMO orbitals with meaningful contribution of  $d_{\rm Ru}$  are LUMO, LUMO+1, LUMO+3 ( $\alpha$ spin) and LUMO+4 (β spin). HOMO-2 and HOMO-3 are localized on the thiocyanate ligands (above 90%) for all the studied compounds.

In the frontier region, neighboring orbitals may show quasidegenerate energy levels. In such cases, consideration of only the HOMO and LUMO may not yield a realistic description of the frontier orbitals. For this reason, the density of states (DOS) and overlap population density of states (OPDOS) in terms of Mulliken population analysis were calculated using the GAUSSSUM program. They provide a pictorial representation of the MO compositions and their contributions to chemical bonding. The DOS and OPDOS diagrams for complexes **1** and **3** are shown in Fig. 5. The DOS plots mainly present the composition of the fragment orbitals contributing to the molecular orbitals. The OPDOS can enable us to ascertain the

#### Table 2

Selected bond lengths (Å) and angles (°) for  $[Ru(SCN)_2(PPh_3)_2(py)_2]$  (1),  $[Ru(SCN)_2(PPh_3)_2(\gamma-pic)_2]$  (2),  $[Ru(SCN)_2(PPh_3)_2(py-2-CH_2NH_2)]$  (3) and  $[Ru(SCN)_2(PPh_3)_2(py-2-CH_2NH_2)]$  (4) with the optimized geometry values.

	1		2		3			4	
	Exp	Calc	Exp	Calc	Exp	Calc		Exp	Calc
Bond lengths (Å)									
Ru(1)-N(1)	2.0460(19)	2.0739	2.023(8)	2.0448	2.079(4)	2.0761	Ru(1) - N(1)	2.033(3)	2.0228
Ru(1) - N(2)	2.0383(19)	2.0717	2.030(9)	2.0452	2.058(5)	2.0468	Ru(1)-N(2)	2.034(3)	2.0433
Ru(1)-N(3)	2.1584(19)	2.2134	2.166(9)	2.1719	2.129(4)	2.1468	Ru(1)-N(3)	2.162(3)	2.1895
Ru(1)-N(4)	2.1537(18)	2.2210	2.179(8)	2.1822	2.136(4)	2.1473	Ru(1)-O(1)	2.216(2)	1.9783
Ru(1) - P(1)	2.3786(6)	2.4517	2.355(3)	2.3931	2.3344(13)	2.3831	Ru(1) - P(1)	2.3077(9)	2.3390
Ru(1)-P(2)	2.3552(6)	2.4513	2.359(3)	2.3952	2.3332(13)	2.3563	Ru(1) - P(2)	2.3318(10)	2.3917
S(1)-C(1)	1.624(3)	1.6321	1.627(10)	1.6243	1.671(9)	1.6214	S(1)-C(1)	1.622(4)	1.6199
N(1)-C(1)	1.156(3)	1.1854	1.171(12)	1.1848	1.144(6)	1.1856	N(1)-C(1)	1.146(4)	1.1859
S(2)-C(2)	1.624(3)	1.6333	1.617(11)	1.6235	1.632(5)	1.6234	S(2)-C(2)	1.636(4)	1.6228
N(2)-C(2)	1.155(3)	1.1849	1.174(13)	1.1852	1.089(9)	1.1839	N(2)-C(2)	1.147(4)	1.1881
Angles (°)									
N(1)-Ru(1)-N(2)	175.86(7)	174.80	174.7(4)	174.87	88.0(2)	91.54	N(1)-Ru(1)-N(2)	171.19(11)	176.51
N(1)-Ru(1)-N(3)	88.99(7)	89.01	89.2(3)	89.17	81.04(17)	80.49	N(1)-Ru(1)-N(3)	83.24(10)	85.63
N(2)-Ru(1)-N(3)	88.47(7)	87.36	87.9(4)	87.58	91.8(2)	91.71	N(2) - Ru(1) - N(3)	90.65(11)	90.88
N(1)-Ru(1)-N(4)	87.96(7)	87.31	86.8(3)	87.29	81.99(17)	81.10	N(1)-Ru(1)-O(1)	89.77(10)	92.34
N(2)-Ru(1)-N(4)	88.42(7)	88.51	88.5(3)	88.29	166.64(18)	168.39	N(2)-Ru(1)-O(1)	82.53(10)	87.00
N(3)-Ru(1)-N(4)	81.02(7)	82.28	83.0(3)	82.59	77.94(16)	78.33	N(3)-Ru(1)-O(1)	75.40(11)	79.19
N(1)-Ru(1)-P(1)	97.59(5)	97.32	88.2(3)	86.98	174.57(13)	172.89	N(1)-Ru(1)-P(1)	99.20(8)	95.91
N(2)-Ru(1)-P(1)	85.69(5)	85.83	96.0(3)	96.59	94.33(15)	94.77	N(2)-Ru(1)-P(1)	87.91(8)	87.44
N(3)-Ru(1)-P(1)	90.38(5)	90.72	87.7(2)	87.79	94.00(12)	93.43	N(3)-Ru(1)-P(1)	98.12(8)	97.01
N(4)-Ru(1)-P(1)	169.71(5)	170.35	169.5(2)	169.00	94.88(12)	94.80	O(1)-Ru(1)-P(1)	168.33(7)	170.65
N(1)-Ru(1)-P(2)	86.97(5)	86.90	96.6(3)	97.12	85.49(13)	83.20	N(1)-Ru(1)-P(2)	87.41(8)	84.50
N(2)-Ru(1)-P(2)	95.00(5)	96.70	85.9(3)	85.98	95.25(19)	96.51	N(2)-Ru(1)-P(2)	96.95(9)	95.90
N(3)-Ru(1)-P(2)	169.79(5)	168.98	171.2(2)	170.75	164.57(12)	163.08	N(3)-Ru(1)-P(2)	163.42(7)	162.06
N(4)-Ru(1)-P(2)	89.47(5)	88.25	90.6(2)	90.88	92.82(11)	92.01	O(1)-Ru(1)-P(2)	90.95(7)	84.58
P(1)-Ru(1)-P(2)	99.43(2)	99.31	99.10(11)	99.27	99.13(4)	99.17	P(1)-Ru(1)-P(2)	96.86(3)	100.15
S(1)-C(1)-N(1)	177.1(2)	178.54	178.7(11)	179.36	177.9(5)	177.86	S(1)-C(1)-N(1)	175.7(4)	177.63
S(2)-C(2)-N(2)	177.7(2)	179.45	176.5(13)	178.25	171.6(16)	171.01	S(2)-C(2)-N(2)	179.9(5)	178.85
Ru(1)-N(1)-C(1)	177.01(18)	173.19	176.5(9)	173.91	175.7(4)	174.46	Ru(1)-N(1)-C(1)	176.0(3)	179.93
Ru(1)-N(2)-C(2)	177.5(2)	173.90	175.5(10)	173.29	173.9(7)	172.98	Ru(1)-N(2)-C(2)	174.7(3)	168.57

bonding, non-bonding and anti-bonding characteristics with respect to particular fragments. A positive value in the OPDOS plots

#### Table 3

D−H···A	d(D-H)	$d(H{\cdot}{\cdot}{\cdot}A)$	$d(D{\cdots}A)$	<(DHA)
1				
$C(8)-H(8)\cdots N(1)$	0.93	2.43	2.984(3)	118.0
$C(14)-H(14)\cdots N(1)$	0.93	2.42	3.166(3)	137.5
$C(3)-H(3)\cdots N(2)$	0.93	2.61	3.065(3)	110.9
$C(12)-H(12)\cdots N(2)$	0.93	2.51	3.017(3)	114.4
C(26)−H(26)···N(2)	0.93	2.59	3.367(3)	140.9
$C(36)-H(36)\cdots N(2)$	0.93	2.59	3.167(3)	120.6
2				
$C(3)-H(3)\cdots N(1)$	0.93	2.45	2.999(15)	117.7
$C(7)-H(7)\cdots N(2)$	0.93	2.50	2.997(15)	113.5
C(13)−H(13)···N(2)	0.93	2.61	3.065(15)	111.0
C(16)−H(16)····N(2)	0.93	2.41	3.066(15)	127.4
$C(40)-H(40)\cdots N(1)$	0.93	2.51	3.253(17)	138.8
$C(46)-H(46)\cdots N(2)$	0.93	2.60	3.358(17)	139.3
3				
$C(7)-H(7)\cdots N(2)$	0.93	2.55	3.102(9)	118.4
$C(22)-H(22)\cdots N(2)$	0.93	2.37	3.154(7)	142.4
$C(32)-H(32)\cdots N(2)$	0.93	2.43	3.224(11)	143.6
$C(32)-H(32)\cdots N(1)$	0.93	2.61	3.101(8)	113.3
C(19)−H(19)···S(1) #1	0.93	2.87	3.481(6)	124.0
4				
C(20)−H(20)···N(1)	0.93	2.50	3.215(5)	133.9
$C(44)-H(44)\cdots N(1)$	0.93	2.55	3.348(5)	144.6
$C(10)-H(10)\cdots N(2)$	0.93	2.50	3.296(5)	143.6
$C(28)-H(28)\cdots N(2)$	0.93	2.55	3.200(5)	127.2
$C(20)-H(20)\cdots N(1)$	0.93	2.50	3.215(5)	133.9

#1 1/2 + x, 3/2 - y, 2 - z.

means a bonding interaction, while a negative value represents an anti-bonding interaction and a value near zero indicates a nonbonding interaction.

As can be see from the OPDOS plots, the thiocyanate ligands have significant anti-bonding character in the HOMO and HOMO–1 molecular orbitals and bonding character in lower HOMO orbitals. The interactions of *N*-heteroaromatic ligands with Ru(II) *d* orbitals have negative values in the frontier HOMO orbitals. In the frontier occupied and virtual molecular orbitals values of the interaction between ruthenium and the studied pyridine compounds indicate the ligands act as strong  $\pi$ -acceptors. This conclusion is confirmed by the mentioned further stabilization energy and Mayer bond orders, which are the following **1**: Ru–P 1.539, 1.553; Ru–N<sub>(py)</sub> 0.724, 0.737; Ru–N<sub>(NCS)</sub> 0.953, 0.944; **2**: Ru–P 1.598, 1.592; Ru–N<sub>(γ-pic)</sub> 0.751, 0.740; Ru–N<sub>(NCS)</sub> 0.980, 0.970; **3**: Ru–P 1.653, 1.636, Ru–N<sub>(py-2-CH2NH2)</sub> 0.740, 0.826; Ru–N<sub>(NCS)</sub> 0.976, 1.77; **4**: Ru–P 0.784, 0.677; Ru–N<sub>(py-2-CH2O)</sub> 0.459; Ru–O 0.872, Ru–N<sub>(NCS)</sub> 0.572, 0.545.

The occupancies of the ruthenium *d* orbitals, obtained from NBO analysis, are as follows **1**:  $d_{xy} - 0.94$ ;  $d_{xz} - 1.83$ ;  $d_{yz} - 1.86$ ;  $d_{x2-y2} - 1.86$ ;  $d_{z2} - 0.83$ , **2**:  $d_{xy} - 0.99$ ;  $d_{xz} - 1.85$ ;  $d_{yz} - 1.85$ ;  $d_{x2-y2} - 1.83$ ;  $d_{zz} - 0.82$ , **3**:  $d_{xy} - 0.99$ ;  $d_{xz} - 1.87$ ;  $d_{yz} - 1.85$ ;  $d_{x2-y2} - 1.81$ ;  $d_{z2} - 0.80$ , **4**:  $d_{xy} - 1.22$ ;  $d_{xz} - 1.53$ ;  $d_{yz} - 1.16$ ;  $d_{x2-y2} - 1.70$ ;  $d_{z2} - 1.31$ . The data suggest that the donation from N-donor ligands to  $d_{Ru}$  orbitals plays a role in the electronic structure of the complexes and to determine the donation, the stabilization energies<sup>1</sup> were calculated. These analyses have shown that the lone pairs localized on the N atom of SCN<sup>-</sup> and py,  $\gamma$ -pic, py-2-CH<sub>2</sub>NH<sub>2</sub> and py-2-CH<sub>2</sub>O

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



Fig. 5. The density of states (DOS) and overlap partial density of states (OPDOS) diagrams for the complexes [Ru(SCN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(py)<sub>2</sub>] (1) and [Ru(SCN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(py-2-CH<sub>2</sub>NH<sub>2</sub>)] (3).

ligands in the studied complexes donate the charge to ruthenium, and the stabilization energies ( $\Delta E_{ij}$ ) are 578.06, 636.4, 598.27, 288.2 kcal/mol and 353.40, 383.63, 406.07, 415.24 kcal/mol for complexes **1**, **2**, **3** and **4**, respectively. The back donation from ruthenium to the *N*-heteroaromatic ligands in the complexes **1**, **2**, **3** and **4** have values 59.71, 61.96, 60.47 and 46.72 kcal/mol, respectively.

The energy decomposition analysis of the studied complexes, based on the work of Morokuma [22] and the extended transition state (ETS) partitioning scheme of Ziegler [23], has been carried out using the ADF program (Release 2008) [24] at the B3LYP/TZP level. The binding energies of the compounds were calculated as the difference between the energy of the complexes with optimized geometries and the energies of the optimized ligands pyridine,  $\gamma$ -picoline, 2-(aminomethyl)pyridine, 2-(hydroxymethyl)pyridine and [Ru(SCN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] fragment. A general theoretical background on the bond energy decomposition scheme can be found in a review paper [25]. In Table 4 the results of energy decomposition analysis calculated for the complexes in the gas phase and more realistically in methanol solvent are listed. As can be seen, the kinetic energies of the studied complexes play an important role for the [Ru(SCN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] – L binding in solution.

In order to make a comparison between the  $\pi$ -acceptor properties of the studied *N*-heteroaromatic ligands, in Fig. 6 the overlap partial density of states (OPDOS) diagrams for the interaction between the central ruthenium ion and the N-donor ligands in the studied complexes are displayed. Taking into account the Mayer bond orders, stabilization energy, values of interactions of N-donor ligands with  $d_{\rm Ru}$  orbitals and bonding energy, the results suggest that pyridine and 2-(hydroxymethyl)pyridine as well  $\gamma$ -picoline and 2-(aminomethyl)pyridine ligands are comparable pairwise in terms of their  $\pi$ -acceptor properties, and pyridine is weakest one.

#### 3.4. Electronic spectra

The complexes presented bands in the UV–Vis spectra resulting from d → d transitions, that are assigned to  ${}^{1}A_{1} \rightarrow {}^{1}T_{1}$  and  ${}^{1}A_{1} \rightarrow {}^{1}T_{2}$  transitions, with maxima at 435.1 nm (22 983 cm<sup>-1</sup>), and 347.5 nm (28 777 cm<sup>-1</sup>) for compound **1**, 405.7 nm (24 649 cm<sup>-1</sup>), 314.1 nm (31 837 cm<sup>-1</sup>) for **2** and 402.4 nm (24 851 cm<sup>-1</sup>), 312.5 nm (31 995 cm<sup>-1</sup>) for complex **3**. The bands attributed to  $\pi^{b}_{C6H6} \rightarrow 3d_{phosphorus}$ ,  $\pi \rightarrow \pi^{*}_{C=C}$  and  $\pi \rightarrow \pi^{*}_{C=N}$  transitions are observed at 238.8, 208.4 nm, 222.6, 212.6 nm and 253.6, 208.7 nm for complexes **1**, **2** and **3**, respectively. The values of the ligand field parameter 10Dq, calculated on the basis of the positions and molar extinction coefficients of electronic bands for the investigated complexes, are equal to 24 380 cm<sup>-1</sup> for **1**, 26 899 cm<sup>-1</sup> for complex **2** and 27 222 cm<sup>-1</sup> for compound **3**. Racah's parameters are equal to  $B = 386 \text{ cm}^{-1}$ , 479 cm<sup>-1</sup>, 476 cm<sup>-1</sup>,  $C = 1537 \text{ cm}^{-1}$ , 1907 cm<sup>-1</sup>, 1896 cm<sup>-1</sup> and the nephelauxetic

Energy decomposition analysis for complexes [Ru(SCN) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> (py) <sub>2</sub> ] (1), [Ru(SCN) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> (γ-pic) <sub>2</sub> ] (2), [Ru(SCN) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> (py-2-CH <sub>2</sub> NH <sub>2</sub> )] (3) and [Ru(SCN) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> (py-2-CH <sub>2</sub> NH <sub>2</sub> )] (4).	20)]
(4) as the $[Ru(SCN)_2(PPh_3)_2]$ fragment and the py, $\gamma$ -pic, py-2-CH <sub>2</sub> NH <sub>2</sub> , py-2-CH <sub>2</sub> O ligands (energies in kcal mol <sup>-1</sup> ).	

Energy (kcal/mol)	$[Ru(SCN)_2(PPh_3)_2(py)_2]$		$[Ru(SCN)_2(PPh_3)_2(\gamma-pic)_2]$		$[Ru(SCN)_2(PPh_3)_2(py-2-CH_2NH_2)]$		[Ru(SCN) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> (py-2-CH <sub>2</sub> O)]	
	Gas phase	CH <sub>3</sub> OH solvent	Gas phase	CH <sub>3</sub> OH solvent	Gas phase	CH <sub>3</sub> OH solvent	Gas phase	CH <sub>3</sub> OH solvent
$\Delta E_{elstat}$	-136.37	-137.71	-154.34	-154.34	-213.12	-213.12	-237.23	-237.23
$\Delta E_{\text{kinetic}}$	240.43	314.67	324.95	395.18	323.31	340.06	397.00	478.68
$\Delta E_{\text{Coulomb (Steric+OrbInt)}}$	-87.09	-139.42	-133.63	-183.65	-151.16	-141.72	-240.23	-301.24
$\Delta E_{XC}$	-81.20	-96.65	-99.06	-113.89	-185.44	-201.96	-111.95	-127.56
$\Delta E_{ m solvation}$		-23.16		-22.68		-40.39		-21.97
$\Delta E$	-64.24	-82.27	-62.09	-79.37	-226.42	-257.13	-192.41	-209.32



Fig. 6. The overlap partial density of states (OPDOS) diagrams for the interaction between the ruthenium central ion and the N-donor ligands in the studied complexes.

parameters are  $\beta_{55}$  = 0.54, 0.67 and 0.66 for compounds **1**, **2** and **3**, respectively. The spectroscopic parameters have been calculated on the basis of the pseudooctahedral geometry of these complexes. The calculations of the C parameter have been based on intercombination transitions  $({}^{1}A_{1} \rightarrow {}^{3}T_{1}; {}^{1}A_{1} \rightarrow {}^{3}T_{2})$  covered by the bands observed in the visible energy region of the spectra.

The ruthenium(III) complex with the 2-(hydroxymethyl)pyridine ligand displayed bands at 510.6, 329.2, 276.6 and 215.0 nm, and for this compound bands are expected in the NIR region. The spectrum in this energy range was not measured and for that reason the 10Dq and Racah's parameters were not determined for the complex. Based on the calculated electronic spectrum, the first experimental band is attributed to HOMO-5/6  $\rightarrow$  LUMO transitions (68%, 34%) and has  $d \rightarrow d$  character with a contribution of  $d \rightarrow \pi^*_{PPh3/Pv-2-CH2O}$  charge transfer transitions. In the energy region adequate to the experimental bands with maxima at 329.2 and 276.6 nm, HOMO  $\rightarrow$  LUMO+1( $\alpha$ )/2( $\beta$ ) (81%) and HOMO  $\rightarrow$  LU-MO+4 (67%), HOMO–23( $\beta$ )  $\rightarrow$  LUMO( $\beta$ ) (64%) transitions were calculated, among others, therefore these bands have MLCT and LMCT character. The highest energy band is assigned to LLCT transitions.

In summary, the four new ruthenium complexes with thiocyanate, triphenylphosphine and N-heteroaromatic ligands have been synthesized and their crystal structures determined. In the structures of all the studied complexes, the triphenylphosphine ligands are in cis positions. The electronic structures of the obtained complexes were calculated. The collected data from NBO, Mayer bond orders and energy decomposition analyses indicate that the  $\pi$ acceptor properties of pyridine and 2-(hydroxymethyl)pyridine, as well as  $\gamma$ -picoline and 2-(aminomethyl)pyridine, are comparable in pairs. The values of the ligand field parameter 10Dg and Racah's parameters were calculated for the studied compounds 1, 2 and 3.

#### 4. Supplementary data

CCDC 758952, 761475, 760151 and 759146 contain the supplementary crystallographic data for the complexes [Ru(SCN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>-(py)<sub>2</sub>], [Ru(SCN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(γ-pic)<sub>2</sub>]·CH<sub>3</sub>OH [Ru(SCN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(py-2-CH<sub>2</sub>NH<sub>2</sub>)] and [Ru(SCN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(py-2-CH<sub>2</sub>O)]·CH<sub>3</sub>OH, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 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 at the Wroclaw Centre for Networking and Supercomputing (http://www.wcss.wroc.pl).

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