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# СИНТЕЗ, СТРУКТУРА И СВОЙСТВА КОМПЛЕКСОВ ПОЗДНИХ ПЕРЕХОДНЫХ МЕТАЛЛОВ С 2-(ТЕТРАЗОЛ-1-ИЛ)ПИРИДИНОМ

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Комплексы состава $[M^{II}(2\text{-pytz})Cl_2]$ (M(II) = Pt, Pd; 2-pytz = 2-(тетразол-1-ил)пиридин) синтезированы прямым взаимодействием 2-pytz с хлоридами соответствующих поздних переходных металлов ($K_2PtCl_4$ или $PdCl_2$). $RuCl_3$ не вступает в реакцию комплексообразования с 2-pytz в среде протонных растворителей, а их кипячение в *N*,*N*-диметилформамиде в присутствии LiCl сопровождается разложением тетразольного цикла и образованием комплексного соединения Ru(III) с производным *N*,*N*-диметил-*N′*-(пиридин-2-ил)формимидамида состава $Li[Ru^{III}(Py—N{=}C—NMe_2)_2Cl_2]$. В результате реакции 2-pytz со специально синтезированным прекурсором *цис*-$[Ru(ДМСО)_4Cl_2]$, где ДМСО – диметилсульфоксид, в метаноле выделен комплекс состава $[Ru(2\text{-pytz})(ДМСО)_3Cl_2] \cdot MeOH$. Взаимодействием *цис*-$[Ru(ДМСО)_4Cl_2]$ с 2-pytz в этаноле получен комплекс состава $[Ru(2\text{-pytz})(ДМСО)_2Cl_2]$. Выделенные продукты охарактеризованы с помощью элементного анализа, масс-спектрометрии с ионизацией электрораспылением и детекцией положительных и отрицательных ионов, инфракрасной спектроскопии, комплексного термического анализа, спектроскопии ядерного магнитного резонанса (ЯМР) на ядрах $^1H$ и $^{13}C$. Структурные параметры комплексов $[Pd(2\text{-pytz})Cl_2]$ и $[Ru(2\text{-pytz})(ДМСО)_3Cl_2] \cdot MeOH$ установлены методом рентгеноструктурного анализа монокристаллов. В структуре $[Pd(2\text{-pytz})Cl_2]$ тетразольный лиганд выступает в качестве *N*,*N*-бидентатно-хелатирующего за счет атома азота пиридинового цикла и атома $N^2$ тетразольного

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кольца, а в структуре [Ru(2-pytz)(ДМСО)$_3$Cl$_2$] · MeOH данный лиганд координирован монодентатно посредством атома N$^4$ тетразольного цикла. Согласно данным ЯМР-спектроскопии на ядрах $^1$H в составе комплекса [Ru(2-pytz)(ДМСО)$_2$Cl$_2$] 2-pytz также выполняет *N*,*N*-бидентатно-хелатирующую функцию и координируется посредством атома азота пиридинового цикла и атома N$^2$ тетразольного кольца.

***Ключевые слова:*** тетразолы; платина(II); палладий(II); рутений(II); металлопромотируемые реакции; координационные соединения; рентгеноструктурный анализ монокристаллов.

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# SYNTHESIS, STRUCTURE AND CHARACTERISATION OF LATE TRANSITION METAL COMPLEXES WITH 2-(TETRAZOL-1-YL)PYRIDINE

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Complexes [M$^{II}$(2-pytz)Cl$_2$] (M(II) = Pt, Pd; 2-pytz = 2-(tetrazol-1-yl)pyridine) were synthesised *via* direct interaction of the corresponding metal chlorides (K$_2$PtCl$_4$ or PdCl$_2$) with 2-pytz under ambient conditions. RuCl$_3$ does not react with 2-pytz under reflux in the protic media, while under reflux in *N*,*N*-dimethylformamide in the presence of LiCl, decomposition of the tetrazole cycle occurred leading to the formation of Ru(III)-coordinated *N*,*N*-dimethyl-*N′*-(pyridin-2-yl)formimidamide derivative Li[Ru$^{III}$(Py—N═C—NMe$_2$)$_2$Cl$_2$]. The complex [Ru(2-pytz)(DMSO)$_3$Cl$_2$] · MeOH, where DMSO is dimethyl sulfoxide, was synthesised by reacting a specially prepared precursor *cis*-[Ru(DMSO)$_4$Cl$_2$] with 2-pytz in methanol under reflux conditions. The complex [Ru(2-pytz)(DMSO)$_2$Cl$_2$] was synthesised by reacting *cis*-[Ru(DMSO)$_4$Cl$_2$] with 2-pytz in ethanol under reflux conditions. The resulting complexes were characterised by elemental analyses, electrospray ionisation mass-spectrometry with detection of positive and negative ions, infrared spectroscopy, $^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectroscopy, and simultaneous thermal analysis. The structures of complexes [Pd(2-pytz)Cl$_2$] and [Ru(2-pytz)(DMSO)$_3$Cl$_2$] · MeOH were investigated by single-crystal X-ray analysis. In the former, 2-pytz shows a N,N-chelating coordination *via* the pyridine ring N and the tetrazole ring N$^2$ atoms. In the latter, 2-pytz coordinates as a monodentate ligand *via* the tetrazole ring N$^4$ atom. According to $^1$H NMR spectroscopy data, in complex [Ru(2-pytz)(DMSO)$_2$Cl$_2$], 2-pytz coordinates as a *N*,*N*-chelating ligand *via* the pyridine ring N and the tetrazole ring N$^2$ atoms.

***Keywords:*** tetrazoles; platinum(II); palladium(II); ruthenium(II); metal-assisted reactions; coordination compounds; single crystal X-ray diffraction.

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## Introduction

Late transition metal complexes based on functionally substituted tetrazoles provide a promising avenue for the design of novel catalysts, luminescent materials and therapeutic agents [1–6]. Pyridyltetrazoles are of interest as potential ligands because their coordination to the metal can be effected by nitrogen atoms belonging both to the tetrazole ring and to the pyridine one. Majority of the up to date reported species are derived from 5-substituted tetrazoles [7; 8]. Also, the interest in 1-substituted tetrazole derivatives is growing. Ligands of this type can be *N*,*N*-chelating or coordinate monodentately *via* N atom of the tetrazole ring [9].

In the present study, we report on synthesis, structure and properties of Pt(II), Pd(II) and Ru(II)-based complexes with a representative N-tetrazolyl substituted pyridine, namely 2-(tetrazol-1-yl)pyridine (2-pytz).

## Materials and methods

Elemental analyses for C, H, and N were performed with FLASH 2000 element analyser (*Thermo Fisher Scientific*, USA). Electrospray ionisation mass-spectra (ESI(+/−)-MS) were registered with LCMS-2020 mass-spectrometer (*Shimadzu*, Japan) using acetonitrile as an eluent. $^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 500 spectrometer (USA). The observed chemical shifts were

referenced to the solvent signals (hexadeuterodimethyl sulfoxide (DMSO-$d^6$), δ, ppm: H 2.50, C 39.43; $D_2O$, δ, ppm: H 4.78; $CD_3CN$, δ, ppm: H 1.94, C 1.32, 118.26). The thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) curves were obtained using a Netzsch STA 429 thermoanalyser (Germany) in a dynamic nitrogen atmosphere (heating rate 10 °C/min, aluminum oxide, mass 1–3 mg). Infrared spectra were recorded on a Thermo Avatar 330 FT – IR system (*Nicolet*, USA) over the 400–4000 $cm^{-1}$ range in SiC cavities.

**X-ray structure determination.** Single crystal X-ray data of complexes $[Pd(2\text{-pytz})Cl_2]$ and $[Ru(2\text{-pytz})(DMSO)_3Cl_2] \cdot MeOH$, where DMSO is dimethyl sulfoxide, were collected on a Smart Apex II diffractometer (*Bruker AXS GmbH*, Germany) using graphite monochromated Mo$K_\alpha$ radiation (λ = 0.710 73 Å). The structures were solved by direct methods (*SIR2014* [10]) and refined on $F^2$ by the full-matrix least squares technique (*SHELXL-2014* [11]). The intensities were corrected for absorption. For both compounds, non-hydrogen atoms were refined anisotropically. Hydrogen atoms were found from difference Fourier map, placed in calculated positions and refined in a «riding» model, with $U_{iso}(H) = 1.5U_{eq}(C)$ for the methyl H atoms and $U_{iso}(H) = 1.2U_{eq}(C)$ for others. Molecular graphics was performed with the program *PLATON* [12].

Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC). Copies of the data can be obtained free of charge on quoting the depository number CCDC 2192259 for $[Pd(2\text{-pytz})Cl_2]$ and 2192260 for $[Ru(2\text{-pytz})(DMSO)_3Cl_2] \cdot MeOH$.

**Synthetic procedures.** 2-Pytz was prepared as reported earlier [6]. $RuCl_3 \cdot H_2O$ (38.9 % of Ru), $PdCl_2 \cdot 2H_2O$ and $K_2PtCl_4$ were received from commercial sources (*Merck*, USA; *Sigma*, USA) and used without further purification. *cis*-$[Ru(DMSO)_4Cl_2]$ was prepared from $RuCl_3 \cdot H_2O$ as reported elsewhere [13]. All the reactions with *cis*-$[Ru(DMSO)_4Cl_2]$ were performed under nitrogen flow.

**$[Pd(2\text{-pytz})Cl_2]$.** A solution of 2-pytz (74 mg, 0.5 mmol) in EtOH was added to the solution of $PdCl_2 \cdot 2H_2O$ (107 mg, 0.5 mmol) in 1 mol/L aqueous HCl. The mixture was stirred at room temperature for 2 h, and the resulting orange-yellow precipitate was filtered off, washed with cold EtOH, and dried in air. The yield of the substance was 80 % (130 mg). Elemental analysis for $[Pd(2\text{-pytz})Cl_2]$ (324.5), %: C. 21.39 (calculated 21.58), H 1.48 (calculated 1.55), N 22.18 (calculated 22.21). ESI(+/−)-MS, *m*/*z*, for $[Pd(2\text{-pytz})Cl(CH_3CN)_2]^+$: 371.90 (calculated 371.98). IR, ν, $cm^{-1}$: 3068.8 s ($\nu(CH)_{aryl}$), 1614.0 s ($\nu(CN)_{py}$), 1489.5 vs ($\nu(CN)_{tz}$), 778.5 s ($\delta_{py}$), 718.3 m ($\delta_{tz}$).

**$[Pt(2\text{-pytz})Cl_2]$.** A solution of 2-pytz (74 mg, 0.5 mmol) in EtOH was added to the solution of $K_2PtCl_4$ (208 mg, 0.5 mmol) in 1 mol/L aqueous HCl. The mixture was stirred at room temperature for 4 h, and the resulting yellow precipitate was filtered off, washed with cold EtOH, and recrystallised from acetonitrile to give pale-yellow crystalline product. The yield of the substance was 54 % (90 mg). Elemental analysis for $[Pt(2\text{-pytz})Cl_2]$ (413.1), %: C 17.63 (calculated 17.44); H 1.12 (calculated 1.22); N 17.11 (calculated 16.95). $^1$H NMR, DMSO-$d^6$, δ, ppm: 10.16 (s, $C5H_{tz}$, 1H), 9.51 (d, $C6H_{py}$, 1H), 8.49 (t, $C5H_{py}$, 1H), 8.15 (d, $C3H_{py}$, 1H), 7.94 (t, $C4H_{py}$, 1H).

**$Li[Ru^{III}(Py—N{=}C—NMe_2)_2Cl_2]$.** A mixture of $RuCl_3 \cdot H_2O$ (152 mg, 0.6 mmol), 2-pytz (166 mg, 1.2 mmol), LiCl (170 mg, 4 mmol) and dimethylformamide (DMF) (10 ml) was heated to reflux with stirring for 6 h. After cooling the solution to room temperature, 40 ml of acetone was added and the mixture was cooled to 0 °C. The resulting yellow crystalline precipitate was collected by filtration and washed with 25 ml of acetone. The yield of the substance was 19.9 % (56 mg). Elemental analysis for $Li[Ru^{III}(Py—N{=}C—NMe_2)_2Cl_2]$ (475.3), %: C 40.28 (calculated 40.43), H 4.62 (calculated 4.24), N 17.75 (calculated 17.68). $^1$H NMR, $D_2O$, δ, ppm: 8.46 (d, $C6H_{py}$, 1H), 7.80 (t-d, $C5H_{py}$, 1H), 7.35 (d, $C3H_{py}$, 1H), 7.11 (t-d, $C4H_{py}$, 1H), 3.23 (s, $CH_{3;NMe_2}$, 3H), 2.71 (s, $CH_{3;NMe_2}$, 3H). ESI(+)-MS, *m*/*z*: 440.09 (calculated 440.06 $[M - Cl^-]^+$), 481.09 (calculated 481.09 $[M - Cl^- + CH_3CN]^+$). ESI(−)-MS, *m*/*z*: 468.00 (calculated 468.02 $[M - Li^+]^-$), 433.00 (calculated 433.05 $[Ru^{II}(Py—N{=}C—NMe_2)_2Cl]^-$), 483.95 (calculated 484.01 $[Ru^{III}(Py—N{=}C—NMe_2)(Py—N{=}C(NMe_2)O)Cl_2]^-$), 500.95 (calculated 501.02 $[Ru^{II}(Py—N{=}C(NMe_2)O)(Py—NH—C(NMe_2){=}O)Cl_2]^-$). IR, ν, $cm^{-1}$: 3168.9 m ($\nu(CH)_{CH_3}$), 1613.9 ($\nu(CN)_{py}$), 1525.0 vs ($\nu(CN)_{NCN}$), 779.8 vs ($\delta_{py}$).

**$[Ru(2\text{-pytz})(DMSO)_3Cl_2] \cdot MeOH$.** A mixture of *cis*-$[Ru(DMSO)_4Cl_2]$ (121 mg, 0.25 mmol), 2-pytz (36 mg, 0.25 mmol) and methanol (30 ml) was heated to reflux with stirring for 3 h under an argon atmosphere. The resulting solution was concentrated to 5 ml. The resulting yellow precipitate was collected by filtration and washed with methanol. The crystals suitable for X-ray analysis were obtained by cooling the filtrate to 0 °C for 3–4 days. The yield of the substance was 24.6 % (36 mg). $^1$H NMR, $CD_3CN$, δ, ppm: 10.22 (s, $C5H_{tz}$, 1H), 8.62 (d-d, $C6H_{py}$, 1H), 8.05–8.09 (m, $C3,5H_{py}$, 2H), 7.58 (m, $C4H_{py}$, 1H), 3.44 (s, $CH_{3;DMSO}$, 6H), 3.35 (s, $CH_{3;DMSO}$, 6H), 3.35 (s, $CH_{3;DMSO}$, 6H). $^{13}$C NMR, $CD_3CN$, δ, ppm: 149.23 ($C5_{py}$), 145.8 ($C1_{py}$), 140.52 ($C3_{py}$), 125.08 ($C2_{py}$), 114.60 ($C4_{py}$), 45.53, 46.52, 46.90 (DMSO). IR, ν, $cm^{-1}$: 3554.0 w br ($\nu(OH)_{MeOH}$), 3010.8 w ($\nu(CH)_{aryl}$), 2925.8 w ($\nu(CH)_{MeOH}$), 1599.1 m ($\nu(CN)_{py}$), 1488.5 s ($\nu(CN)_{tz}$), 786.4 s ($\delta_{py}$), 718.4 m ($\delta_{tz}$), 1083.4 vs ($\nu(SO)_{DMSO}$).

**[Ru(2-pytz)(DMSO)$_2$Cl$_2$].** A mixture of *cis*-[Ru(DMSO)$_4$Cl$_2$] (121 mg, 0.25 mmol), 2-pytz (129 mg, 0.875 mmol) and ethanol (30 ml) was heated to reflux with stirring for 3 h under an argon atmosphere. The resulting solution was concentrated to 5 ml. The resulting yellow-orange precipitate was collected by filtration and washed with methanol. The yield of the substance was 28.7 % (44 mg). $^1$H NMR, $CD_3CN$, δ, ppm: 10.43 (d, C6H$_{py}$, 1H), 10.09 (s, C5H$_{tz}$, 1H), 8.29 (t-d, C5H$_{py}$, 1H), 8.20 (d, C3H$_{py}$, 1H), 7.58 (m, C4H$_{py}$, 1H), 3.57 (s, CH$_{3;DMSO}$, 6H), 3.48 (s, CH$_{3;DMSO}$, 6H). $^{13}$C NMR, $CD_3CN$, δ, ppm: 154.12 (C5$_{py}$), 143.83 (C1$_{py}$), 141.15 (C3$_{py}$), 125.71 (C2$_{py}$), 114.63 (C4$_{py}$), 45.84 (DMSO), 43.13 (DMSO). IR, ν, cm$^{-1}$: 3093.3 m (ν(CH)$_{aryl}$), 1597.8 m (ν(CN)$_{py}$), 1469.1 s (ν(CN)$_{tz}$), 773.1 s (δ$_{py}$), 717.6 m (δ$_{tz}$), 1080.4 vs (ν(SO)$_{DMSO}$).

## Results and discussion

**Preparation of the complexes.** 2-Pytz ligand was found to readily react with platinum and palladium chlorides (namely, $K_2PtCl_4$ and $PdCl_2$) in water-ethanol mixtures to give [M(2-pytz)Cl$_2$] complexes (M = Pt, Pd), regardless of the metal to ligand ratio utilised (fig. 1). The products were isolated as light-yellow crystalline powders and characterised by elemental analyses, ESI(+)-MS, IR spectroscopy, $^1$H and $^{13}$C NMR spectroscopy, and simultaneous thermal analysis. The molecular and crystal structure of [Pd(2-pytz)Cl$_2$] was established by single crystal X-ray diffraction analysis (XRD).

In order to investigate coordination properties of 2-pytz toward Ru(II) as an octahedral metal center, a series of the earlier reported synthetic approaches has been attempted. In this regard, interaction of 2-pytz with the most popular Ru(II) precursors, such as Ru(III) chloride and *cis*-[Ru(DMSO)$_4$Cl$_2$], was investigated under various reaction conditions and at different metal to ligand ratios (from 1 : 1 to 1 : 3.5).

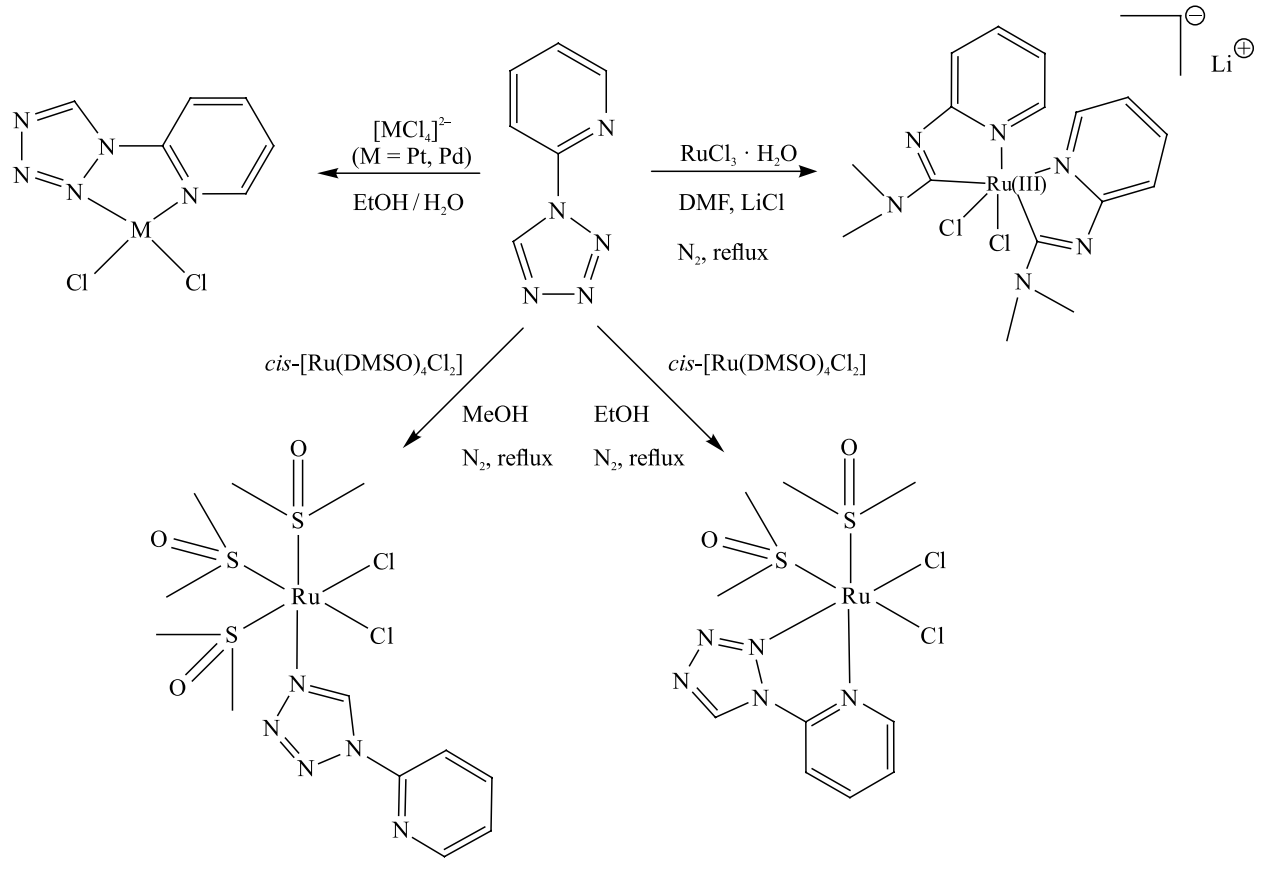


*Fig. 1.* Synthesis of 2-pytz complexes with Pt(II), Pd(II), and Ru(II/III) chlorides

Direct interaction of diimine heterocyclic ligands with $RuCl_3$ under reflux in ethanol, ethanol-water mixtures, and DMF has been widely reported as an efficient method of Ru(II)-based chelates preparation [8]. This method is applicable to 2,2′-bipyridine, its derivatives, some bisthiazoles, bisimidazoles, etc. [14; 15]. Moreover, it has recently been utilised for the synthesis of Ru(II)-based homoleptic complexes with 2-(2-alkyltetrazol-5-yl)pyridines [6].

In our study, it was shown that 2-pytz did not react with $RuCl_3$ under relatively mild conditions, i. e. under reflux in methanol or ethanol solutions. This may be due to spatial inability of 2-pytz to form stable chelate cycle with the central Ru ion *via* the most basic $N^4$ atom of the tetrazole ring [16] as it is possible for 2,5-functionalised tetrazole derivatives (fig. 2).

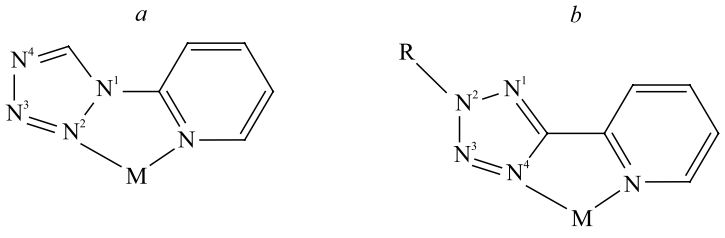


*Fig. 2.* The structure of the chelate cycle for 2-pytz (*a*) and 2-(2-R-tetrazol-5-yl)pyridines (*b*)

Interaction of $RuCl_3$ with 2-pytz under harsher conditions, i. e. under reflux in DMF in the presence of LiCl, led to formation of a bright-yellow crystalline powder insoluble in DMF, DMSO, acetonitrile and chlorinated solvents, partially soluble in water and hot ethanol. The isolated product was characterised by elemental analysis, ESI(+/–)-MS, IR and $^1$H NMR spectroscopy, and thermal analysis. The results of $^1$H NMR spectroscopy point out to the decomposition of the tetrazole cycle and the presence of two non-equivalent methyl groups in the structure of the product. Based on the overall data, the following molecular formula was proposed $Li[Ru^{III}(Py—N{=}C—NMe_2)_2Cl_2]$ for the obtained complex (see fig. 1), that is lithium salt of the anionic Ru(III) complex containing two C-deprotonated *N*,*N*-dimethyl-*N*′-(pyridin-2-yl)formimidamide moieties as bidentate C,N-chelating ligands and two chlorido ligands in the ruthenium inner coordination sphere.

As depicted in fig. 3, the plausible mechanism of *N*,*N*-dimethyl-*N*′-(pyridin-2-yl)formimidamide formation includes three steps. In the first step, thermal decomposition of the 1-substituted tetrazole with formation of *N*-(pyridin-2-yl)cyanamide proceeds. Thermal decomposition of 1-substituted tetrazoles with formation of cyanamides under reflux in DMF solution in the presence of metal salts and also in their absence have been described earlier in the literature [17; 18]. At the second stage, cyanamide is hydrolysed with formation of 2-aminopyridine. Hydrolysis of cyanamides usually proceeds in the presence of water in acidic media [19; 20]. In our case, this process is possible due to the presence of trace amounts of water from $RuCl_3 \cdot H_2O$ and most probably is Ru-catalysed. The last step includes Ru-assisted condensation of 2-aminopyridine and DMF molecule to give coordinated *N*′-(pyridin-2-yl)formimidamide. The similar transformation has recently been reported for the 2-aminopyrazine derivative under heating in DMF in the sealed tube in the presence of CuI as a catalyst [21].

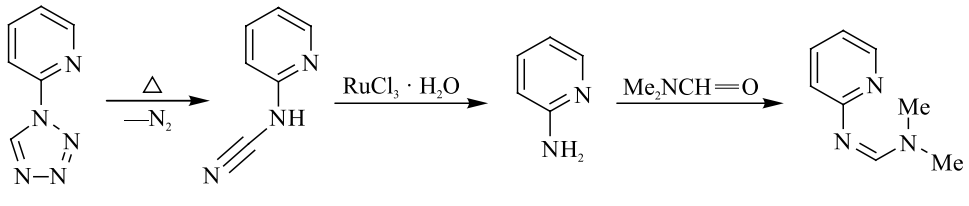


*Fig. 3.* The proposed mechanism of *N*,*N*-dimethyl-*N*′-(pyridin-2-yl)formimidamide formation

The attributed formula is consistent with the data of elemental analysis, $^1$H NMR spectroscopy and ESI-MS. In the $^1$H spectrum of the compound, the two singlets were observed at 3.23 and 2.71 ppm and assigned to the non-equivalent N-bound $CH_3$ groups, that appeared noticeably shifted in comparison with the spectrum of free *N*,*N*-dimethyl-*N*′-(pyridin-2-yl)formimidamide in $D_2O$ (3.02 and 2.91 ppm, respectively [22]). The absence in the spectrum of the complex of any noticeable signal attributable to azomethine CH proton (observed in the spectrum of the free formimidamide at 7.94 ppm [22]) testifies to the deprotonation of formimidamide moiety upon coordination with formation of the anionic Ru(III) species.

The latter conclusion was also consistent with the ESI(+/–)-MS of the complex. Thus, the signal at $m/z = 468.00$ was observed in the ESI(–)-MS and assigned to $[M - Li^+]^-$ anion (fig. 4, *a*), while the signals at $m/z = 440.09$ and 481.09 detected in the ESI(+)-MS of the complex were attributed to $[M - Cl^-]^+$ and $[M - Cl^- + CH_3CN]^+$ ions (calculated $m/z = 440.06$ and $m/z = 481.09$, respectively). The signal at $m/z = 433.00$ in the ESI(–)-MS was assigned to the Ru(II) species $[Ru^{II}(Py—N{=}C—NMe_2)_2Cl]^-$ (fig. 4, *b*) that can be explained either by the presence of Ru(II)-coordinated complex $Li_2[Ru^{II}(Py—N{=}C—NMe_2)_2Cl_2]$ as a minor impurity in the main Ru(III)-based

product or by reduction of Ru(III) species in the mass-spectrometer due to lability of Ru(II)/Ru(III) redox pair. The presence of the signals at $m/z = 483.95$ and $m/z = 500.95$ in the ESI(–)-MS of the complex was attributed to the hydrolysis of the coordinated formimidamide moiety in the presence of water as a part of eluting mixture. As shown in fig. 4, the above signals were assigned to ions $[Ru^{III}(Py—N=C—NMe_2)(Py—N=C(NMe_2)O)Cl_2]^-$ and $[Ru^{II}(Py—N=C(NMe_2)O)(Py—NH=C(NMe_2)=O)Cl_2]^-$ with the calculated $m/z$ values of 484.01 and 501.02, respectively.

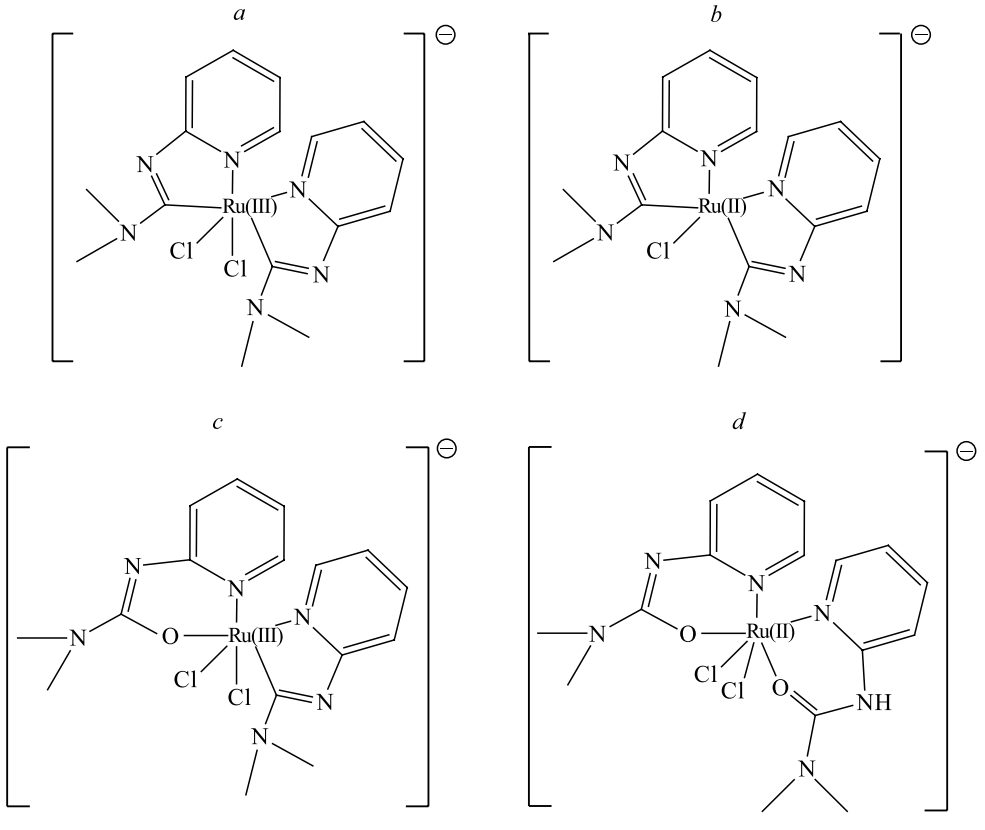


*Fig. 4.* The structural formulas of the ions detected in the ESI(–)-MS of $Li[Ru^{III}(Py—N=C—NMe_2)_2Cl_2]$ with the calculated $m/z$ values of 468.02 (*a*), 433.05 (*b*), 484.01 (*c*), 501.02 (*d*)

Since preparation of Ru(II) complexes with 2-pytz *via* its direct interaction with $RuCl_3$ was found unsuccessful, we further attempted an alternative synthetic procedure that implied interaction of the nitrogenous ligand with a specially prepared Ru(II) precursor, i. e. *cis*-$[Ru(DMSO)_4Cl_2]$. *cis*-$[Ru(DMSO)_4Cl_2]$ is known as a well-behaved Ru(II) precursor [23], and its behaviour in reactions with a variety of nitrogen-based ligands, including heterocyclic derivatives, is well documented [24]. However, no information is present in the literature on the reactivity of *cis*-$[Ru(DMSO)_4Cl_2]$ towards tetrazole derivatives.

2-Pytz was found to react with *cis*-$[Ru(DMSO)_4Cl_2]$ under reflux in methanol or ethanol solutions (see fig. 1). In methanol, reaction leads to the exchange of the *O*-coordinated DMSO molecule with formation of $[Ru(2\text{-pytz})(DMSO)_3Cl_2] \cdot MeOH$ as well defined light-yellow crystals suitable for single crystal XRD analysis. This result is consistent with the previously published data on reactivity of *cis*-$[Ru(DMSO)_4Cl_2]$ and explained by increased lability of *O*-coordinated DMSO molecule in the *trans*-position to *S*-bound DMSO [24].

In ethanol, substitution of the two adjacent DMSO molecules with 2-pytz acting as a bidentate chelating ligand occurs leading to the formation of $[Ru(2\text{-pytz})(DMSO)_2Cl_2]$ as an orange crystalline product. Formation of this complex was observed irrespective of the metal to ligand ratio applied (from 1 : 1 to 1 : 3.5). However, in the presence of excess of 2-pytz, the isolated product contained a significant admixture of the unreacted ligand, and all attempts of its purification either through recrystallisation or *via* column chromatography failed.

The isolated tetrazole-containing Ru(II) complexes were characterised by elemental analyses, IR and NMR spectroscopy, simultaneous thermal analysis. Molecular and crystal structure of $[Ru(2\text{-pytz})(DMSO)_3Cl_2] \cdot MeOH$ was established by single crystal XRD analysis.

**Characterisation of the 2-pytz complexes.** According to the data of X-ray diffraction analysis, Pt and Pd complexes are isotypic and, therefore, display almost identical IR spectra. Notably, coordination leads to a significant simplification of the vibrational spectra of 2-pytz in the complexes in comparison with the spectrum of the free ligand. Despite the differences in the suggested coordination mode, all the studied complexes demonstrate very similar spectra in the region of the stretching and deformational vibrations of the tetrazole-containing ligand. Thus, strong or medium bands at 1599–1618 and 778 $cm^{-1}$ were assigned to the ν(C═N) stretching and $\delta_{py}$ deformational vibrations of the pyridine cycle, respectively. The bands at 1488–1491 and 713–718 $cm^{-1}$ were associated with the ν(C═N) stretching and $\delta_{tz}$ deformational vibrations of the tetrazole cycle, correspondingly. Importantly, the latter bands are lacking in the IR spectrum of $Li[Ru^{III}(Py—N═C—NMe_2)_2Cl_2]$ formed as a result of 2-pytz decomposition in boiling DMF (*vide supra*). In the IR spectra of $[Ru(2\text{-pytz})(DMSO)_3Cl_2] \cdot MeOH$ and $[Ru(2\text{-pytz})(DMSO)_2Cl_2]$, the strong bands of stretching ν(S═O) vibrations are additionally observed at approximately 1080–1083 $cm^{-1}$, pointing out to the presence of the *S*-coordinated DMSO molecules [13].

Pt(II) and Ru(II) complexes were additionally characterised by $^1H$ and $^{13}C$ NMR spectroscopy. The $^1H$ NMR spectrum of $[Pt(2\text{-pytz})Cl_2]$ displays the set of signals of 2-pytz that is noticeably shifted downfield in comparison with the spectrum of the free ligand, indicating participation of both rings in coordination. According to the data of $^1H$ NMR spectroscopy, the Pt complex was unstable in DMSO-$d^6$ solution releasing free 2-pytz ligand upon dissolution. This fact is rather unusual for other cisplatin analogues, that commonly experience substitution of chlorido ligands for DMSO, but retain *N*-coordinated ligands, including N-substituted tetrazole derivatives [25].

Table 1

**The chemical shifts of 2-pytz protons in the $^1H$ NMR spectra of free 2-pytz and its Pt(II) and Ru(II) complexes**

| Compound | Solvent | δ, ppm | | | | |
|---|---|---|---|---|---|---|
| | | $C5H_{tz}$ | $C3H_{py}$ | $C4H_{py}$ | $C5H_{py}$ | $C6H_{py}$ |
| 2-Pytz | DMSO-$d^6$ | 10.18 (s) | 8.06 (d) | 7.64 (t) | 8.19 (t) | 8.66 (d) |
| $Pt(2\text{-pytz})Cl_2$ | | 10.16 (s) | 8.15 (d) | 7.94 (t) | 8.49 (t) | 9.51 (d) |
| 2-Pytz | $CD_3CN$ | 9.63 (s) | 8.05 (d) | 7.53 (m) | 8.09 (m) | 8.58 (d) |
| $[Ru(2\text{-pytz})(DMSO)_3Cl_2] \cdot MeOH$ | | 10.22 (s) | 8.07 (d) | 7.60 (m) | 8.12 (m) | 8.62 (d) |
| $[Ru(2\text{-pytz})(DMSO)_2Cl_2]$ | | 10.08 (s) | 8.18 (d) | 7.78 (t) | 8.28 (t) | 10.42 (d) |

The $^1H$ NMR spectrum of $[Ru(2\text{-pytz})(DMSO)_3Cl_2]$ reveals three singlets in the region 3.39–3.44 ppm indicating the presence of three coordinated DMSO molecules. As follows from the data summarised in table 1, a significant downfield shift of the tetrazole C5H proton signal is observed in the spectrum of this complex at 10.22 ppm as compared to the spectrum of the ligand (9.63 ppm), while the signals of the pyridine cycle protons were only marginally changed. This is in consistence with the suggested monodentate coordination mode of the 2-pytz ligand *via* $N^4$ atom of the tetrazole ring. As demonstrated by the $^1H$ NMR data, this complex is unstable in the acetonitrile solution and undergoes decomposition with the release of free 2-pytz.

In accord with the assigned formula, the $^1H$ NMR spectrum of $[Ru(2\text{-pytz})(DMSO)_2Cl_2]$ exhibits only two singlets in the region of 3.47–3.56 ppm indicating the presence of two coordinated DMSO molecules in its molecular structure. In this case, involvement of the pyridine N atom in coordination is evidenced by a significant downfield shift of the doublet signal corresponding to the C6H proton of the pyridine ring from 8.58 to 10.42 ppm. Based on these data, a bidentate *N*,*N*-chelating mode of 2-pytz coordination was proposed for this compound with $N^2$ atom of the tetrazole ring situated in the equatorial plane of the Ru(II) distorted octahedral coordination sphere and the pyridine N atom occupying the apical *trans*-position to *S*-coordinated DMSO molecule.

According to the TG and DSC data, Pt and Pd complexes are thermally stable up to 200 °C and decompose exothermally without melting at approximately 220–280 °C (fig. 5), whereas the Ru(II) complexes are less stable and start to decompose at approximately 120–140 °C (fig. 6). Lower thermal stability of Ru(II)-based

compounds is probably due to the presence of coordinated DMSO molecules. For instance, decomposition of $[Ru(2\text{-pytz})(DMSO)_3Cl_2] \cdot MeOH$ starts with a loss of MeOH molecule, which is followed by the endothermal peak at approximately 140 °C with a weight loss of approximately 11 %. The latter was assigned to the loss of one of the coordinated DMSO molecules (calculated weight loss is 13.3 %). Further two-step exothermal decomposition proceeds at 180–350 °C and was assigned to the decomposition of 2-pytz as well as coordinated DMSO molecules. Similar two-step exothermal decomposition of $[Ru(2\text{-pytz})(DMSO)_2Cl_2]$ occurs at 140–340 °C and is preceded by melting observed as an endothermal peak without weight loss at 127 °C. For both Ru(II) complexes, formation of metal sulfide as the final product of thermal decomposition was observed as evidenced by the decomposition residue weights and further confirmed by X-ray powder analysis of the residues.

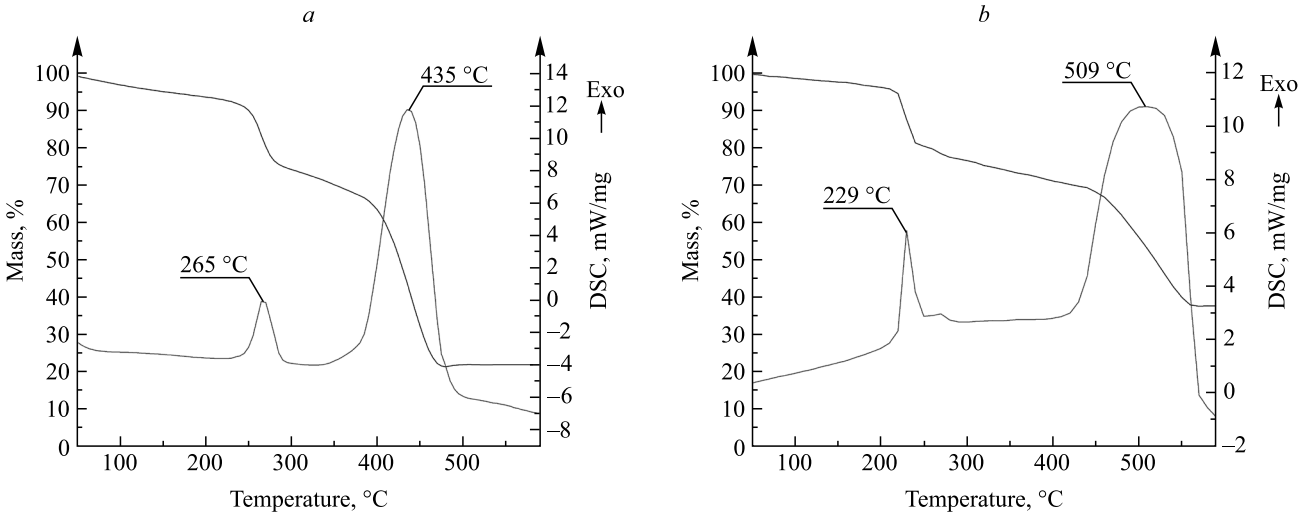


*Fig. 5.* DSC and TG curves of $[Pd(2\text{-pytz})Cl_2]$ (*a*) and $[Pt(2\text{-pytz})Cl_2]$ (*b*)

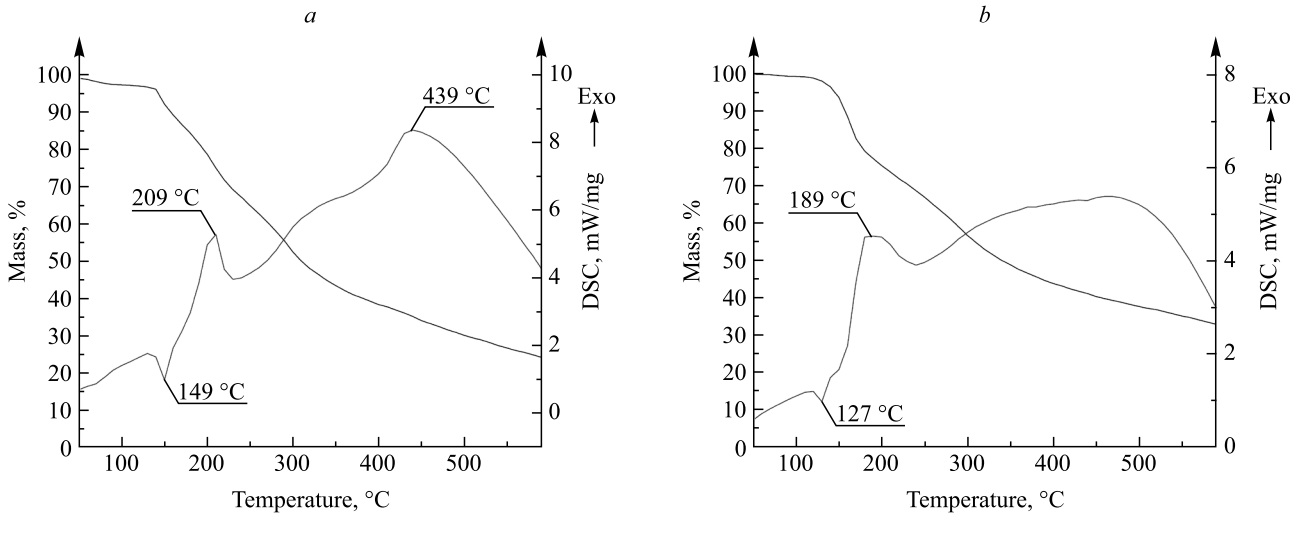


*Fig. 6.* DSC and TG curves of $[Ru(2\text{-pytz})(DMSO)_3Cl_2] \cdot MeOH$ (*a*) and $[Ru(2\text{-pytz})(DMSO)_2Cl_2]$ (*b*)

**X-ray structure determination of $[Pd(2\text{-pytz})Cl_2]$ and $[Ru(2\text{-pytz})(DMSO)_3Cl_2] \cdot MeOH$.** Molecular and crystal structures of $[Pd(2\text{-pytz})Cl_2]$ and $[Ru(2\text{-pytz})(DMSO)_3Cl_2] \cdot MeOH$ were established by single crystal XRD analysis at the temperature of 100 K. Crystal data, data collection, and structure refinement details for both compounds are summarised in table 2.

Table 2

**Main crystallographic data and structure refinement details for complexes [Pd(2-pytz)$Cl_2$] and [Ru(2-pytz)$(DMSO)_3Cl_2$] · MeOH**

| Parameter | [Pd(2-pytz)$Cl_2$] | [Ru(2-pytz)$(DMSO)_3Cl_2$] · MeOH |
|---|---|---|
| Formula | $C_6H_5Cl_2N_5Pd$ | $C_{13}H_{27}Cl_2N_5O_4RuS_3$ |
| Formula weight | 324.45 | 585.54 |
| Temperature, K | 100(2) | 100(2) |
| Wavelength, Å | 0.710 73 | 0.710 73 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | *C*2/*c* | $P2_1/c$ |
| *a*, Å | 16.5217(8) | 9.05360(10) |
| *b*, Å | 7.3160(4) | 15.9560(2) |
| *c*, Å | 16.9906(8) | 16.5396(2) |
| α, deg | 90 | 90 |
| β, deg | 103.5594(13) | 104.1928(3) |
| γ, deg | 90 | 90 |
| *V*, Å$^3$ | 1996.46(17) | 2316.37(5) |
| *Z* | 8 | 4 |
| $d_{calc}$, g · cm$^{-3}$ | 2.159 | 1.679 |
| μ, mm$^{-1}$ | 2.359 | 1.206 |
| Crystal size, mm | 0.22 × 0.14 × 0.13 | 0.27 × 0.25 × 0.24 |
| Number of | | |
| measured reflections | 45 179 | 147 256 |
| independent reflections | 4413 [$R_{int}$ = 0.019 3] | 8086 [$R_{int}$ = 0.018 0] |
| refined parameters | 127 | 261 |
| Goodness-of-fit on $F^2$ | 1.103 | 1.118 |
| $R_1$, $wR_2$ [$I > 2\sigma(I)$] | $R_1$ = 0.014 4, $wR_2$ = 0.033 6 | $R_1$ = 0.017 0, $wR_2$ = 0.041 2 |
| $R_1$, $wR_2$ [all data] | $R_1$ = 0.014 9, $wR_2$ = 0.033 8 | $R_1$ = 0.018 2, $wR_2$ = 0.041 8 |
| CCDC | 2192259 | 2192260 |

N o t e. *Z* is a number of formula units in unit cell; $d_{calc}$ is a calculated density; μ is a linear absorption coefficient; $R_1$ and $wR_2$ are discrepancy factors.

**[Pd(2-pytz)$Cl_2$]**. This complex is a molecular complex, crystallising in the monoclinic space group *C*2/*c*, with eight complex molecules in the unit cell and one molecule in the asymmetric unit. All atoms are in general positions. The molecule of the complex is presented in fig. 7. The palladium atom shows slightly distorted square environment, formed by two chlorine atoms in *cis*-positions and one ligand molecule coordinated in chelate mode at the expense of the tetrazole ring N2 and the pyridine ring N5 atoms. The coordination core [$PdCl_2N_2$] is very flat, being planar within 0.0058(4) Å. Coordination bond lengths and angles in the complex are given in table 3. As can be seen, coordination bond lengths take the expected values. Among adjacent coordination angles, the angle N2—Pd1—N5 is the smallest because of chelate coordination of 2-pytz ligand. Least squares planes of the tetrazole and pyridine rings in the ligand molecule are inclined at a small angle of 3.56(5)°. The tetrazole ring bond lengths are typical of 1-substituted tetrazoles, with the shortest bond N2—N3 in the ring (see fig. 7).

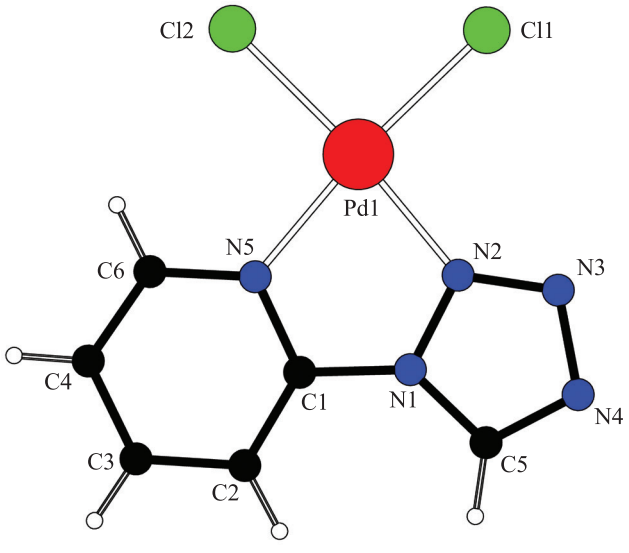


*Fig. 7.* Complex molecule of [Pd(2-pytz)$Cl_2$] with the atom-numbering scheme. The tetrazole ring bond lengths, Å: N1—C5 = 1.3425(12), N1—N2 = 1.3508(11), N2—N3 = 1.2924(11), N3—N4 = 1.3561(12), N4—C5 = 1.3268(13)

Table 3

**Coordination bond lengths and angles in complex [Pd(2-pytz)$Cl_2$]**

| Bond | Bond length, Å |
|---|---|
| Pd1—N2 | 2.0016(8) |
| Pd1—N5 | 2.0434(8) |
| Pd1—Cl2 | 2.2699(2) |
| Pd1—Cl1 | 2.2798(2) |

| Bond | Angles, deg |
|---|---|
| Cl1—Pd1—Cl2 | 91.102(9) |
| Cl1—Pd1—N2 | 94.45(2) |
| Cl2—Pd1—N5 | 94.79(2) |
| N2—Pd1—N5 | 79.66(3) |
| Cl1—Pd1—N5 | 174.09(2) |
| Cl2—Pd1—N2 | 174.44(2) |

There are non-classic hydrogen bonds in the crystal structure of [Pd(2-pytz)$Cl_2$], all hydrogen atoms of the complex participating in them (table 4). The only intramolecular hydrogen bond is C6—H6···Cl2, whereas all others are intermolecular ones forming hydrogen-bonded three-dimensional network. There are also weak $\pi - \pi$ stacking interactions in the complex (fig. 8). They occur between two pyridine rings of neighbouring molecules at ($x$, $y$, $z$) and ($1 - x$, $1 - y$, $1 - z$), with inter-centroid distance Cg···Cg = 3.832 0(6) Å and the dihedral angle between the rings $\alpha = 0°$.

Crystal packing of complex [Pd(2-pytz)$Cl_2$] is shown in fig. 9.

Table 4

**Hydrogen bonds geometry in the crystal structures of [Pd(2-pytz)$Cl_2$]**

| D—H···A | D—H, Å | H···A, Å | D···A, Å | D—H···A, deg |
|---|---|---|---|---|
| C2—H2···Cl2[a] | 0.95 | 2.69 | 3.5850(10) | 157 |
| C3—H3···N3[b] | 0.95 | 2.62 | 3.2467(13) | 124 |
| C4—H4···Cl1[b] | 0.95 | 2.78 | 3.6741(10) | 158 |
| C5—H5···Cl1[a] | 0.95 | 2.67 | 3.4593(10) | 141 |
| C5—H5···Cl2[a] | 0.95 | 2.83 | 3.6595(10) | 147 |
| C6—H6···Cl2 | 0.95 | 2.69 | 3.2738(10) | 120 |

Note. Symmetry codes: $x, -y+1, z-\frac{1}{2}$ ([a]); $x+\frac{1}{2}, y+\frac{1}{2}, z$ ([b]).

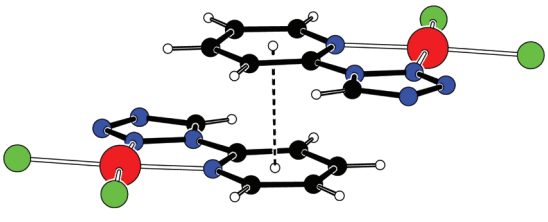

*Fig. 8.* π – π Stacking interactions in the crystal structure of [Pd(2-pytz)$Cl_2$]

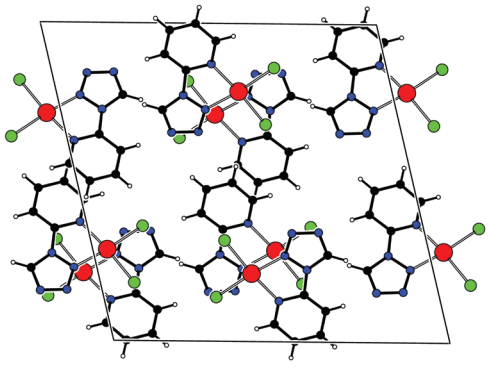

*Fig. 9.* Crystal structure of [Pd(2-pytz)$Cl_2$] viewed along *b* axis

**[Ru(2-pytz)(DMSO)$_3$Cl$_2$] · MeOH.** According to X-ray data, this coordination compound includes complex molecules [Ru(2-pytz)(DMSO)$_3$Cl$_2$] together with co-crystallised methanol molecules. The complex crystallises in the monoclinic space group $P2_1/c$, with four formula units in the unit cell and one molecule in the asymmetric unit. All atoms of the compound occupy general positions. Complex molecule is shown in fig. 10 together with MeOH molecule.

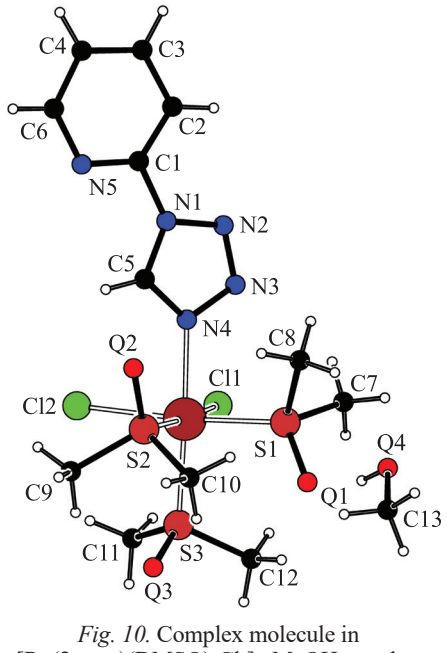


*Fig. 10.* Complex molecule in [Ru(2-pytz)(DMSO)$_3$Cl$_2$] · MeOH together with co-crystallised methanol molecule. The tetrazole ring bond lengths, Å: N1—C5 = 1.3365(11), N1—N2 = 1.3570(11), N2—N3 = 1.2869(11), N3—N4 = 1.3709(11), N4—C = 1.3196(11)

The Ru1 atom is surrounded by one ligand 2-pytz, coordinated *via* the tetrazole ring $N^4$ atom, two chlorine atoms in *cis*-position, and three DMSO molecules, coordinated through the sulfur atoms. Coordination bond lengths are given in table 5. Their comparison with the literature data indicates that the Ru1—N4 bond of 2.1142(8) Å in complex [Ru(2-pytz)(DMSO)$_3$Cl$_2$] · MeOH is in the range with the previously reported Ru-tetrazole complexes (2.044(4)–2.010(4) Å [6] and 2.104(3)–2.110(2) Å [26]).

It should be noted that the tetrazole and pyridine rings in 2-pytz are inclined at 3.71(5)°, being close to that in complex [Pd(2-pytz)$Cl_2$]. The tetrazole ring bond lengths are typical of 1-substituted tetrazoles, with the shortest bond N2—N3 in the ring (see fig. 10).

There are various hydrogen bonds in the crystal structure of complex [Ru(2-pytz)(DMSO)$_3$Cl$_2$] · MeOH. They include classic and non-classic, intra- and intermolecular H-bonds (table 6). All intramolecular H-bonds are non-classic, formed by DMSO hydrogen atoms. These are C—$H_{DMSO}$···$N_{tz}$ (No. 5), C—$H_{DMSO}$···Cl (No. 9, 13, 14), and C—$H_{DMSO}$···$O_{DMSO}$ (No. 8, 10, 15). All other hydrogen bonds are intermolecular. Among them, there are those of pyridine H atoms C—$H_{py}$··· Cl (No. 2) and C—$H_{py}$···$O_{DMSO}$ (No. 3), and also the bonds of DMSO hydrogen atoms C—$H_{DMSO}$···Cl (No. 4, 11), C—$H_{DMSO}$···$O_{DMSO}$ (No. 12, 15), and C—$H_{DMSO}$···$O_{methanol}$ (No. 6, 7). The latter bonds of methanol O atom, together with classic bond O—$H_{methanol}$···$O_{DMSO}$ (No. 1) of the methanol H atom held the methanol molecules in the crystal structure of the compound.

Table 5

**Coordination bond lengths in complex [Ru(2-pytz)(DMSO)$_3$Cl$_2$] · MeOH**

| Bond | Bond length, Å |
|---|---|
| Ru1—N4 | 2.1142(8) |
| Ru1—S1 | 2.2599(2) |
| Ru1—S2 | 2.2851(2) |
| Ru1—S3 | 2.2909(2) |
| Ru1—Cl2 | 2.4111(2) |
| Ru1—Cl1 | 2.4159(2) |

There are also two types of weak π – π stacking interactions in the crystal structure of [Ru(2-pytz)(DMSO)$_3$Cl$_2$] · MeOH (fig. 11). One of them takes place between two pyridine rings of two neighbouring molecules at ($x$, $y$, $z$) and ($2 - x$, $1 - y$, $2 - z$), with inter-centroid distance Cg···Cg = 4.0467(6) Å and the dihedral angle between the rings α = 0°. Other interaction occurs between the tetrazole ring at ($x$, $y$, $z$) and pyridine ring at ($2 - x$, $1 - y$, $2 - z$), with inter-centroid distance Cg···Cg = 3.7603(5) Å and the dihedral angle between the rings α = 3.71(5)°.

Crystal packing of complex [Ru(2-pytz)(DMSO)$_3$Cl$_2$] · MeOH is shown in fig. 12.

Table 6

**Hydrogen bonds geometry in the crystal structures of [Ru(2-pytz)(DMSO)$_3$Cl$_2$] · MeOH**

| Bond number | D—H···*A* | D—H, Å | H···A, Å | D···A, Å | D—H···A, deg |
|---|---|---|---|---|---|
| 1 | O4—H4···O1 | 0.84 | 2.02 | 2.8280(14) | 160 |
| 2 | C3—H3···Cl2[a] | 0.95 | 2.78 | 3.4245(10) | 126 |
| 3 | C6—H6···O2[c] | 0.95 | 2.51 | 3.3586(13) | 149 |
| 4 | C7—H7C···Cl2[b] | 0.98 | 2.81 | 3.4358(12) | 122 |
| 5 | C8—H8B···N3 | 0.98 | 2.56 | 3.1317(15) | 117 |
| 6 | C8—H8B···O4[e] | 0.98 | 2.53 | 3.3047(16) | 136 |
| 7 | C8—H8C···O4 | 0.98 | 2.56 | 3.3894(17) | 143 |
| 8 | C9—H9B···O3 | 0.98 | 2.32 | 3.1186(15) | 138 |
| 9 | C9—H9C···Cl2 | 0.98 | 2.73 | 3.2292(13) | 112 |
| 10 | C10—H10B···O3 | 0.98 | 2.59 | 3.3210(15) | 131 |
| 11 | C10—H10C···Cl1[f] | 0.98 | 2.64 | 3.5426(12) | 153 |
| 12 | C11—H11A···O2[d] | 0.98 | 2.30 | 3.2469(14) | 162 |
| 13 | C11—H11B···Cl1 | 0.98 | 2.79 | 3.3714(12) | 119 |
| 14 | C11—H11C···Cl2 | 0.98 | 2.68 | 3.2734(12) | 120 |
| 15 | C12—H12A···O1 | 0.98 | 2.40 | 3.1336(15) | 131 |

Note. Symmetry codes: $2 - x, 1 - y, 2 - z$ ([a]); $x, \frac{3}{2} - y, -\frac{1}{2} + z$ ([b]); $1 - x, 1 - y, 2 - z$ ([c]); $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$ ([d]); $1 - x, 1 - y, 1 - z$ ([e]); $-1 + x, y, z$ ([f]).

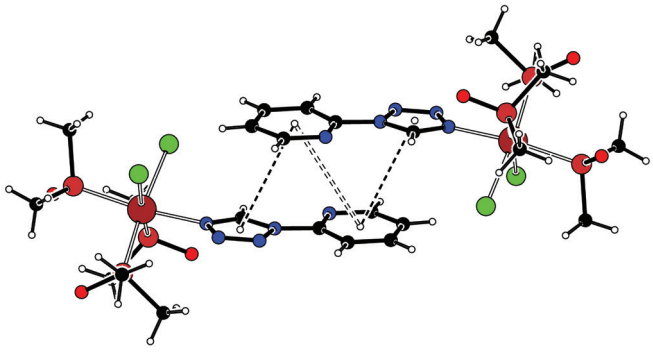

*Fig. 11*. π – π Stacking interactions in the crystal structure of [Ru(2-pytz)$(DMSO)_3Cl_2$] · MeOH

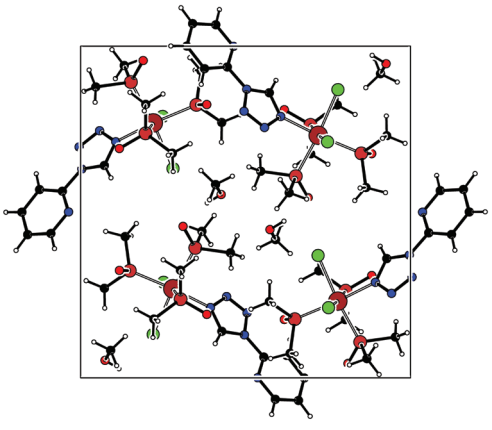

*Fig. 12.* Crystal packing of [Ru(2-pytz)$(DMSO)_3Cl_2$] · MeOH, viewed along the *a* axis

## Conclusion

In the present study, interaction of 2-(tetrazol-1-yl)pyridine with a series of late transition metal halides was investigated. It was shown that Pt(II) and Pd(II) chlorides react with 2-pytz with formation of chelated complexes [M(2-pytz)$Cl_2$]. $RuCl_3$ does not react with 2-pytz under mild conditions, while under reflux in DMF solution the reaction is accompanied by decomposition of the tetrazole cycle with formation of anionic Ru(III)-coordinated *N*,*N*-dimethyl-*N*′-(pyridin-2-yl)formimidamide derivative $Li[Ru^{III}(Py—N{=}C—NMe_2)_2Cl_2]$. The proposed mechanism of formation of the above product includes thermal decomposition of 2-(tetrazol-1-yl)pyridine to give *N*-(pyridin-2-yl)cyanamide, its hydrolysis resulting in 2-aminopyridine and Ru-assisted condensation of the latter with DMF molecule. Two octahedral tetrazole-containing Ru(II) complexes, namely [Ru(2-pytz)$(DMSO)_3Cl_2$] · MeOH and [Ru(2-pytz)$(DMSO)_2Cl_2$], were prepared by reacting *cis*-[Ru$(DMSO)_4Cl_2$] with 2-pytz in methanol or ethanol. Molecular and crystal structures of [Ru(2-pytz)$(DMSO)_3Cl_2$] · MeOH and [Pd(2-pytz)$Cl_2$] were established by single crystal X-ray diffraction. In the former, 2-pytz coordinates as a monodentate ligand *via* $N^4$ atom of the tetrazole ring, while in complex [Pd(2-pytz)$Cl_2$], 2-pytz coordinates as a *N*,*N*-chelating ligand *via* the pyridine ring N and the tetrazole ring $N^2$ atoms. The *N*,*N*-chelating mode of 2-pytz coordination was also proposed for [Ru(2-pytz)$(DMSO)_2Cl_2$] based on the data of $^1$H NMR spectroscopy. Thus, we can conclude that coordination properties of this ligand depend both on metal ion and reaction conditions.

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