# Rhodium(III) Complexes with 2-(2'-Pyridyl)quinoline. Synthesis and Spectroscopic Characterization 

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#### Abstract

Rhodium(III) complexes containing 2-(2'-pyridyl)quinoline (PQ) were prepared by the reaction of $\mathrm{RhCl}_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ and PQ in 1:2 mole ratio followed by addition of an excess of sodium salts to

Keywords rhodium(III) complexes 2-(2'-pyridyl)quinoline the reaction mixture. The new complexes cis- $\left[\mathrm{RhX}_{2}(\mathrm{PQ})_{2}\right] \mathrm{Y}$ (where $\mathrm{X}=\mathrm{NO}_{2}{ }^{-}, \mathrm{Y}=\mathrm{PF}_{6}{ }^{-} ; \mathrm{X}=$ $\mathrm{SCN}^{-}$or $\mathrm{NO}_{3}^{-}$, $\left.\mathrm{Y}=\mathrm{Cl}^{-} ; \mathrm{X}=\mathrm{Y}=\mathrm{I}^{-}\right)$and cis- $\left[\mathrm{Rh}\left(\mathrm{N}_{3}\right)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}(\mathrm{PQ})\right] \mathrm{PF}_{6}$ were characterized by elemental analysis, conductivity measurements, IR, ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR.


## INTRODUCTION

The coordination chemistry of rhodium(III) is currently of great interest, since some of these complexes have been found to posses antitumor activity ${ }^{1}$ and can be used as potential models for a number of important catalytic systems. ${ }^{2}$

The coordination compounds of $\alpha$-diimines such as 2-(2'-pyridyl)quinoline (PQ) (Figure 1) are the subject of continuous and intense research, especially as model complexes for biochemical studies. ${ }^{3,4}$

The significant role of 2-(2'-pyridyl)quinoline as an $\alpha$-diimine ligand, along with the importance of rhodium(III) complexes as antibacterial and antitumor, ${ }^{5 \mathrm{a}}$ and mu-

trans
tagenic agents, ${ }^{5 \mathrm{~b}}$ prompted us to prepare and characterize rhodium(III) complexes of 2-(2'-pyridyl)quinoline. Elemental analysis, conductivity measurements, FT-IR, ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR of these complexes are presented and discussed.

## EXPERIMENTAL

## Materials

The ligand 2-(2'-pyridyl)quinoline was prepared according to a previously reported method. ${ }^{6}$ All chemicals used in the study were of analytical grade, obtained from common vendors and used as commercially supplied without further purification.

cis

Figure 1. Structure of 2-(2'-pyridyl)quinoline, PQ.

## Instrumentation

M-H-W Laboratories, Phoenix, Arizona, USA, performed the elemental analyses for $\mathrm{C}, \mathrm{H}, \mathrm{N}$, and S . IR spectra were taken on a Mattson 5000 FT-IR spectrophotometer in the range 4000 to $500 \mathrm{~cm}^{-1}$ as KBr pellets and on a PYE-Unicam SP3-3000 spectrophotometer as CsI pellets in the range 500 to $200 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR were conducted on a Bruker AC-200 NMR spectrometer. Chemical shifts were referenced to TMS. All NMR spectra were obtained in deuterated dimethylsulfoxide ( $\mathrm{DMSO}-\mathrm{d}_{6}$ ). Conductivity measurements were done with a Jenway conductivity meter model 4010 at $25{ }^{\circ} \mathrm{C}$ using $1.0 \times 10^{-3} \mathrm{M}$ solutions in $N, N$ dimethylformamide (DMF). Melting points were obtained using an electrothermal melting point apparatus.

## Preparation of Complexes

$\left[\mathrm{Rh}\left(\mathrm{NO}_{2}\right)_{2}\left(\mathrm{PQ}_{2}\right)_{2}\right] P F_{6}$ and $\left[\mathrm{Rh}\left(\mathrm{N}_{3}\right)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}(P Q)\right] P F_{6}$. - The complexes were prepared by mixing stoichiometric amounts of $\mathrm{RhCl}_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ and ligand PQ in a 1:2 ratio in aqueous (5 mL ) and ethanolic ( 4 mL ) solutions, respectively. A small amount of hydrazine dihydrochloride ( 0.06 g ) was added to the mixture. The mixture was stirred at room temperature for 2 h and then a 2 mL aqueous solution of sodium nitrite ( 14 mmol ), or sodium azide ( 10 mmol ), was added dropwise under constant stirring. The whole reaction mixture was refluxed for $2-5 \mathrm{~h}$, then the solution was filtered and left at room temperature for cooling. The filtrate was treated with a saturated aqueous solution of $\mathrm{NH}_{4} \mathrm{PF}_{6}$, affording a precipitate immediately. The products were collected by filtration, washed with ethanol and ether, and dried under vacuum at $40^{\circ} \mathrm{C}$.

$$
\left[\mathrm{RhX}_{2}(\mathrm{PQ})_{2}\right] \mathrm{Cl}\left(\mathrm{X}=\mathrm{SCN}^{-}, \mathrm{NO}_{3}^{-}\right) .-\mathrm{PQ}(0.45 \mathrm{mmol})
$$ was added to a solution of $\mathrm{RhCl}_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}(0.23 \mathrm{mmol})$ in 5 mL of water and the mixture was stirred at room temperature for 2 h . A small amount of hydrazine dihydrochloride $(0.06 \mathrm{~g})$ was added and the mixture was stirred at room temperature for an additional 2 h . To the resulting yellow solution, an aqueous solution ( 2 mL ) containing 10 mmol of NaSCN or $\mathrm{NaNO}_{3}$ was added dropwise under constant stirring. The solution was refluxed for $2-5 \mathrm{~h}$ to give a product, which was filtered off, washed with ethanol and ether, and dried under vacuum at $40^{\circ} \mathrm{C}$.

$\left[R h I_{2}(P Q)_{2}\right] I$. - The same procedure as described for $\left[\mathrm{Rh}(\mathrm{SCN})_{2}(\mathrm{PQ})_{2}\right] \mathrm{Cl}$ was used for the preparation of this complex, but the mole ratio of $\mathrm{RhCl}_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}: \mathrm{PQ}: \mathrm{NaI}$ was 1:2:40.

## RESULTS AND DISCUSSION

## Preparation and Physical Properties of the Complexes

Rhodium(III) complexes of 2-(2'-pyridyl)quinoline (PQ) were prepared by the reaction of PQ with $\mathrm{RhCl}_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ in the 2:1 mole ratio and an excess of sodium salts NaX ( $\mathrm{X}=\mathrm{NO}_{2}^{-}, \mathrm{SCN}^{-}, \mathrm{NO}_{3}^{-}, \mathrm{I}^{-}$and $\mathrm{N}_{3}^{-}$). The complexes were obtained in low to good yields (40-90 \%). Hydrazine dihydrochloride was used as catalyst for the synthesis of complexes with cis configuration. ${ }^{7}$ The synthetic routes used for the preparation of rhodium(III) complexes are shown in Scheme 1.


Scheme 1.

All isolated products are colored solids, stable in air, soluble in DMF and DMSO and insoluble in water and common organic solvents. The molar conductivity values for $1.0 \times 10^{-3} \mathrm{M}$ solutions presented in Table I confirm their behaviour as $1: 1$ electrolytes. ${ }^{9}$ These results are consistent with the octahedral structures (Figure 2)

TABLE I. Analytical and physical data for the complexes

| Complex | Anal. calcd. (found) / \% |  |  | M.p. | Color | $\Lambda_{\mathrm{M}}{ }^{(\mathrm{a})}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | C | H | N | ${ }^{\circ} \mathrm{C}$ |  | $\mathrm{S} \mathrm{cm}{ }^{2} \mathrm{~mol}^{-1}$ |
| $\left[\mathrm{Rh}\left(\mathrm{NO}_{2}\right)_{2}(\mathrm{PQ})_{2}\right] \mathrm{PF}_{6}$ | 44.70 (45.11) | 2.68 (2.45) | 11.17 (10.80) | 292 | Yellow | 69 |
| $\left[\mathrm{Rh}(\mathrm{SCN})_{2}(\mathrm{PQ})_{2}\right] \mathrm{Cl}^{(\mathrm{b})}$ | 54.02 (53.72) | 3.02 (2.89) | 12.60 (12.10) | 222 | Orange-yellow | 67 |
| $\left[\mathrm{Rh}\left(\mathrm{NO}_{3}\right)_{2}(\mathrm{PQ})_{2}\right] \mathrm{Cl}$ | 49.83 (48.67) | 2.99 (2.86) | 12.46 (11.76) | 243 | Yellow | 76 |
| $\left[\mathrm{RhI}_{2}(\mathrm{PQ})_{2}\right] \mathrm{I}$ | 37.53 (38.04) | 2.25 (2.22) | 6.25 (6.23) | 233 | Red-brown | 72 |
| $\left[\mathrm{Rh}\left(\mathrm{N}_{3}\right)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2} \mathrm{PQ}\right] \mathrm{PF}_{6}$ | 29.30 (30.80) | 2.46 (2.57) | 19.50 (19.81) | 190 | Yellow | 81 |

[^0]

A


B


C


D


E


Figure 2. Possible structures of complexes.
proposed for the cationic species $\left[\mathrm{RhX}(\mathrm{PQ})_{2}\right]^{+}$where X $=\mathrm{NO}_{2}^{-}, \mathrm{SCN}^{-}, \mathrm{NO}_{3}^{-}, \mathrm{I}^{-}$(Figure 2; $\mathbf{A}, \mathbf{B}$, or $\mathbf{C}$ ) and $\left[\mathrm{Rh}\left(\mathrm{N}_{3}\right)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2} \mathrm{PQ}\right] \mathrm{PF}_{6}$ (Figure 2; $\mathbf{D}$ or $\mathbf{E}$ ).

## IR Spectroscopy

Characteristic IR bands (Table II) were assigned on the basis of earlier studies made on 2-(2'-pyridyl)quinoline and similar diimine ligands. ${ }^{7,8}$ As it has been reported, the nitrogen donor atoms in the free ligand are in a trans position in order to minimize steric repulsion between the $\mathrm{H}\left(3,3^{\prime}\right)$ protons. Upon coordination, they adopt a cis configuration (Figure 1)..$^{7,8}$

In the spectra of isolated complexes, the main regions showing appreciable changes with respect to the spectrum of the free PQ ligand are between 1685-1470 $\mathrm{cm}^{-1}(v(\mathrm{C}=\mathrm{C})$ and $v(\mathrm{C}=\mathrm{N})$ absorptions $)$ and $850-730 \mathrm{~cm}^{-1}$ $\gamma(\mathrm{C}-\mathrm{H})$ bands. In general, these characteristic bands are in all the complexes (Table II) shifted upwards, as compared to PQ. Based on previously reported results, ${ }^{7,10}$ such an increase in frequency and the reduction of intensity prove the involvement of the pyridine nitrogen donor atoms in bonding to rhodium.

The spectra were also examined in the low frequency region where metal-ligand $(v(\mathrm{Rh}-\mathrm{X}))$ bands appear. In-
spection of the spectra for all complexes (Table II) revealed the following features:
(i) The IR spectra of $\left[\mathrm{Rh}\left(\mathrm{NO}_{2}\right)_{2}(\mathrm{PQ})_{2}\right] \mathrm{PF}_{6}$ and $\left[\mathrm{Rh}\left(\mathrm{N}_{3}\right)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2} \mathrm{PQ}\right] \mathrm{PF}_{6}$ show strong bands at $\approx 845 \mathrm{~cm}^{-1}$ and $557 \mathrm{~cm}^{-1}$ assigned to the stretching vibrations of the $\mathrm{P}-\mathrm{F}$ bond, indicating the presence of an ionic $\mathrm{PF}_{6}{ }^{-}$ group. ${ }^{11 a}$
(ii) The appearance of bands at 1433, 1422, 1341, and $1316 \mathrm{~cm}^{-1}$ for $\left[\mathrm{Rh}\left(\mathrm{NO}_{2}\right)_{2}(\mathrm{PQ})_{2}\right] \mathrm{PF}_{6}$ supports the presence of coordinated nitro $\left(-\mathrm{NO}_{2}\right)$ rather than nitrito (-ONO) group. ${ }^{11 b}$
(iii) The complex $\left[\mathrm{Rh}(\mathrm{SCN})_{2}(\mathrm{PQ})_{2}\right] \mathrm{Cl}$ gives a very strong band at $2124 \mathrm{~cm}^{-1}$ due to the CN stretching vibrations and two bands of medium intensity at 721 and 468 $\mathrm{cm}^{-1}$, which may be attributed to the $v(\mathrm{CS})$ and $\delta(\mathrm{NCS})$ absorptions, respectively. These bands confirm the presence of the Rh-SCN bond. ${ }^{11 \mathrm{c}}$ Furthermore, the ligand bands in the region $850-730 \mathrm{~cm}^{-1}$ are reduced in intensity upon complexation, which is a further evidence for coordination of PQ to $\mathrm{Rh}^{\text {III }}$.
(iv) The three bands at 1420,1335 , and $1027 \mathrm{~cm}^{-1}$ in the spectrum of $\left[\mathrm{Rh}\left(\mathrm{NO}_{3}\right)_{2}(\mathrm{PQ})_{2}\right] \mathrm{Cl}$ strongly confirm the presence of a monodentate rather than the chelating bidentate $\mathrm{NO}_{3}{ }^{-}$group. ${ }^{11 \mathrm{~d}}$

TABLE II. Important $\mathbb{R}$ frequencies for the ligand and complexes. $\operatorname{IR}(\mathbf{K B r} \& C s \mid) / \mathrm{cm}^{-1}($ a)

| Complex | $v(\mathrm{C}=\mathrm{C})$ and $v(\mathrm{C}=\mathrm{N})$ | $\gamma(\mathrm{C}-\mathrm{H})$ | $v(\mathrm{Rh}-\mathrm{X})$ |
| :---: | :---: | :---: | :---: |
| 2-(2'-Pyridyl)quinoline (PQ) | 1597 vs, 1555 m, $1503 \mathrm{~s}, 1490$ s, 1420 s | 847 s, 796 s 779 vs, 743 vs |  |
| $\left[\mathrm{Rh}\left(\mathrm{NO}_{2}\right)_{2}(\mathrm{PQ})_{2}\right] \mathrm{PF}_{6}{ }^{\text {(b) }}$ | 1520 s, 1508 s, 1489 s, 1446 s | 773 s | 370 m, 348 m split |
| $\left[\mathrm{Rh}(\mathrm{SCN})_{2}(\mathrm{PQ})_{2}\right] \mathrm{Cl}{ }^{\text {(c) }}$ | 1636 vs, 1558 s, $1520 \mathrm{~s}, 1487 \mathrm{~s}, 1456 \mathrm{~m}$ | $831 \mathrm{~m}, 771 \mathrm{~s}$ | 375 m, 350 m split |
| $\left[\mathrm{Rh}\left(\mathrm{NO}_{3}\right)_{2}(\mathrm{PQ})_{2}\right] \mathrm{Cl}{ }^{\text {(d) }}$ | $\begin{aligned} & 1684 \mathrm{~m}, 1638 \mathrm{~s}, 1618 \mathrm{~s}, 1558 \mathrm{~m}, 1541 \mathrm{~m}, \\ & 1520 \mathrm{~m} 1487 \mathrm{~m}, 1458 \mathrm{~m} \end{aligned}$ | 790 w, 773 m | $405 \mathrm{~m}, 390 \mathrm{~m}$ split |
| $\left[\mathrm{RhI}_{2}(\mathrm{PQ})_{2}\right] \mathrm{I}$ | 1637 vs, 1618 vs, $1541 \mathrm{~s}, 1508 \mathrm{~s}, 1458 \mathrm{~m}$ | 771 m | $\mathrm{NA}^{(\mathrm{f})}$ |
| $\left[\mathrm{Rh}\left(\mathrm{N}_{3}\right)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2} \mathrm{PQ}\right] \mathrm{PF}_{6}{ }^{(\mathrm{e})}$ | $\begin{aligned} & 1683 \mathrm{~s}, 1637 \mathrm{~s}, 1618 \mathrm{~s}, 1558 \mathrm{~s}, 1541 \mathrm{vs} \text {, } \\ & 1520 \mathrm{~s}, 1474 \mathrm{~s} \end{aligned}$ | 779 m, 742 w | $\begin{aligned} & 545 \mathrm{~m}, 520 \mathrm{w} \\ & 460 \mathrm{~m} 445 \mathrm{w} \end{aligned}$ |

[^1](v) The complex $\left[\mathrm{Rh}\left(\mathrm{N}_{3}\right)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}(\mathrm{PQ})\right] \mathrm{PF}_{6}$ exhibits two very strong bands at 2125 and $2030 \mathrm{~cm}^{-1}$, which could be attributed to $v\left(\mathrm{~N}_{3}\right) \cdot{ }^{11 \mathrm{e}}$ The appearance of a broad band of medium intensity in the range $3440-3410 \mathrm{~cm}^{-1}$, in addition to the bands between $1625-1610 \mathrm{~cm}^{-1}$, indicates the presence of water molecules in the complex. ${ }^{11 \mathrm{f}}$ Furthermore, the two bands present at 545 and $520 \mathrm{~cm}^{-1}$ in the spectrum of the same complex might be ascribed to the $\mathrm{Rh}-\mathrm{OH}_{2}$ stretching vibration, ${ }^{11 \mathrm{f}}$ whereas the split band at 460 and $445 \mathrm{~cm}^{-1}$ may be attributed to the $v\left(\mathrm{Rh}-\mathrm{N}_{3}\right)$ modes. ${ }^{11 \mathrm{e}}$ The multiplicity of the $\mathrm{Rh}-\mathrm{O}$ and Rh $-\mathrm{N}_{3}$ stretching bands strongly supports cis-aqua and cis-azide arrangement in this complex, as shown in Figure 2 ( $\mathbf{D}$ or $\mathbf{E}$ ).

As a conclusion of the above discussion, the low frequency region ( $500-200 \mathrm{~cm}^{-1}$ ) of the IR spectra could give an insight into structural configuration of the new complexes. Normally, the appearance of split metal-ligand bands in this region in the spectra of all the complexes (Table II) is a strong evidence for the cis rather than trans configuration. ${ }^{7,8}$ In addition, the method of synthesis, using hydrazine hydrochloride as a catalyst, ${ }^{7}$ along with other physical measurements (see NMR section), further supports the cis configuration of the diimine ligand in the new complexes.

## ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR Spectroscopy

The ${ }^{1} \mathrm{H}$ NMR spectral data of the 2-(2'-pyridyl)quinoline and its complexes are given in Table III. Assignment was made according to similar results found for previously reported complexes and other related diimine ligands. ${ }^{7,8}$ The changes in chemical shifts for resonances of protons in the spectra of complexes with respect to those
in the free ligand may be related to the deshielding effect of the metal due to its anisotropy and to the change of the electron density in the aromatic ring of PQ . The most dramatic changes show the $\mathrm{H}(8)$ and $\mathrm{H}\left(6^{\prime}\right)$ protons, which are not equivalent in the two ligand molecules bonded to the metal (Table III).

One $\mathrm{H}(8)$ and one $\mathrm{H}\left(6^{\prime}\right)$ proton, which are directed toward ligands X (see Figure 2) are the most deshielded protons showing the greatest downfield shift. They are found as doublets in the range $10.60-8.80(\operatorname{area} 1 \mathrm{H})$ and 10.35-8.60 (area 1 H ) with a coupling constant of 6.0-4.4 and $8.0-5.5 \mathrm{~Hz}$, respectively. These results are consistent with the structure shown in Figure 3 (equivalent to structure $\mathbf{A}$ in Figure 2), and the results obtained for the $\mathrm{Hg}^{2+}, \mathrm{Pd}^{2+}$, and $\mathrm{Pt}^{2+}$ complexes of $\mathrm{PQ} .{ }^{8,14}$

Structures $\mathbf{B}$ and $\mathbf{C}$ in Figure 2 are excluded because they are expected to show one doublet for the equivalent two $\mathrm{H}\left(6^{\prime}\right)$ and one for the equivalent two $\mathrm{H}(8)$ protons, or two doublets each with the same coupling constant. ${ }^{8}$


Figure 3. Proposed structure of $\left[\operatorname{Rh} X_{2}(\mathrm{PQ})_{2}\right]^{+}$complexes.

TABLE III. ${ }^{1}$ H NMR characteristics of 2-(2'-pyridyl)quinoline and its complexes ${ }^{\left({ }^{(a)}\right)}$

| Compound | $\delta / \mathrm{ppm}(\mathrm{J} / \mathrm{Hz})$ |
| :---: | :---: |
| 2-(2'-Pyridyl)quinoline (PQ) ${ }^{\text {(b) }}$ | $\begin{aligned} & 8.76(\mathrm{~d}, 1 \mathrm{H}, J=4.8), 8.62(\mathrm{~d}, 1 \mathrm{H}, J=8.1), 8.58(\mathrm{dd}, 1 \mathrm{H}, J=1.5,8.6), 8.51(\mathrm{~m}, 1 \mathrm{H}), \\ & 8.13(\mathrm{~d}, 1 \mathrm{H}, J=8.6), 8.02(\mathrm{dt}, 2 \mathrm{H}, J=1.6,8.1), 7.82(\mathrm{t}, 1 \mathrm{H}, J=7.6), 7.65(\mathrm{t}, 1 \mathrm{H}, \\ & J=7.6), 7.53(\mathrm{t}, 1 \mathrm{H}, J=6.4) . \end{aligned}$ |
| $\left[\mathrm{Rh}\left(\mathrm{NO}_{2}\right)_{2}(\mathrm{PQ})_{2}\right] \mathrm{PF}_{6}$ | $\begin{aligned} & 9.69(\mathrm{~d}, 1 \mathrm{H}, J=5.5), 9.46(\mathrm{~d}, 1 \mathrm{H}, J=5.8), 9.24-8.77(\mathrm{~m}, 2 \mathrm{H}), 8.74(\mathrm{t}, 4 \mathrm{H}, J=7.2) \text {, } \\ & 8.64-8.42(\mathrm{~m}, 2 \mathrm{H}), 8.23(2 \mathrm{~d}, 2 \mathrm{H}, J=8.6), 8.07(\mathrm{~d}, 2 \mathrm{H}, J=8.2), 7.84-7.63(\mathrm{~m}, 3 \mathrm{H}), \\ & 7.54(\mathrm{t}, 2 \mathrm{H}, J=6.4), 6.97(\mathrm{t}, 1 \mathrm{H}, J=7.2) \end{aligned}$ |
| $\left[\mathrm{Rh}(\mathrm{SCN})_{2}(\mathrm{PQ})_{2}\right] \mathrm{Cl}$ | $\begin{aligned} & 9.86(\mathrm{~d}, 1 \mathrm{H}, J=4.6), 9.75(\mathrm{~d}, 1 \mathrm{H}, J=5.5), 9.20-9.10(2 \mathrm{~d}, 1 \mathrm{H}, J=8.3), 9.06-8.94 \\ & (\mathrm{~m}, 3 \mathrm{H}), 8.80-8.68(2 \mathrm{~d}, 4 \mathrm{H}, J=8.6), 8.46-8.05(\mathrm{~m}, 5 \mathrm{H}), 7.80-7.64(\mathrm{~m}, 2 \mathrm{H}), 7.45 \\ & (\mathrm{t}, 1 \mathrm{H}, J=7.6), 7.10(\mathrm{t}, 2 \mathrm{H}, J=6.8) . \end{aligned}$ |
| $\left[\mathrm{Rh}\left(\mathrm{NO}_{3}\right)_{2}(\mathrm{PQ})_{2}\right] \mathrm{Cl}$ | $\begin{aligned} & 9.90(\mathrm{~d}, 1 \mathrm{H}, J=4.4), 9.77(\mathrm{~d}, 1 \mathrm{H}, J=5.5), 9.19-9.08(2 \mathrm{~d}, 1 \mathrm{H}, J=8.3), 9.04-8.92 \\ & (\mathrm{~m}, 3 \mathrm{H}), 8.78-8.65(2 \mathrm{~d}, 4 \mathrm{H}, J=9.3), 8.45-8.03(\mathrm{~m}, 5 \mathrm{H}), 7.80-7.64(\mathrm{~m}, 2 \mathrm{H}), 7.43 \\ & (\mathrm{t}, 1 \mathrm{H}, J=7.6), 7.07(\mathrm{t}, 2 \mathrm{H}, J=6.8) . \end{aligned}$ |
| $\left[\mathrm{RhI}_{2}(\mathrm{PQ})_{2}\right] \mathrm{I}$ | $\begin{aligned} & 10.60(\mathrm{~d}, 1 \mathrm{H}, J=5.3), 10.35(\mathrm{~d}, 1 \mathrm{H}, J=6.5), 9.10-8.78(\mathrm{~m}, 1 \mathrm{H}), 8.70-8.36(\mathrm{~m}, 6 \mathrm{H}), \\ & 8.30-8.00(\mathrm{~m}, 6 \mathrm{H}), 7.80-7.62(\mathrm{~m}, 2 \mathrm{H}), 7.54-7.38(\mathrm{~m}, 2 \mathrm{H}), 6.88(\mathrm{t}, 1 \mathrm{H}, J=7.0) . \end{aligned}$ |
| $\left[\mathrm{Rh}(\mathrm{PQ})\left(\mathrm{N}_{3}\right)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right] \mathrm{PF}_{6}$ | $\begin{aligned} & 8.80(\mathrm{~d}, 1 \mathrm{H}, J=6.1), 8.60-8.53(\mathrm{~m}, 3 \mathrm{H}), 8.19-8.05(\mathrm{~m}, 3 \mathrm{H}), 7.86(\mathrm{t}, 1 \mathrm{H}, J=7.5), \\ & 7.69(\mathrm{t}, 1 \mathrm{H}, J=5.4), 7.58(\mathrm{t}, 1 \mathrm{H}, J=7.8) . \end{aligned}$ |

[^2]TABLE IV. ${ }^{13} \mathrm{C}$ NMR characteristics of 2-(2'-pyridyl)quinoline and its complexes ${ }^{(a)}$

| Compound | $\delta / \mathrm{ppm}$ |
| :---: | :---: |
| 2-(2'-Pyridyl)quinoline (PQ) ${ }^{(\mathrm{b})}$ | $155.4,155.2,149.3,147.2,137.4,137.2,130.0,129.2,128.0,127.9,127.0,124.6,121.1$ $118.4 .$ |
| $\left[\mathrm{Rh}\left(\mathrm{NO}_{2}\right)_{2}(\mathrm{PQ})_{2}\right] \mathrm{PF}_{6}$ | 158.7, 157.9, 157.5, 157.2, 156.4, 155.6, 154.5, 154.1, 150.5, 147.2, 146.1, 144.6, 143.4, $143.3,142.9,132.9,132.2,130.2,130.1,129.8,129.7,128.3,128.0,127.2,126.7,123.8$, 120.5, 119.6. |
| $\left[\mathrm{Rh}(\mathrm{SCN})_{2}(\mathrm{PQ})_{2}\right] \mathrm{Cl}$ | $160.0,159.2,158.9,157.8,157.5,157.2,153.6,152.9,150.8,148.5,147.1,147.0,143.3$, $142.8,142.0,132.9,132.3,130.6,129.9,129.6,129.4,129.1,127.7,127.5,126.9,123.9$, 123.7, 120.6, 117.5, 117.2. |
| $\left[\mathrm{Rh}\left(\mathrm{NO}_{3}\right)_{2}(\mathrm{PQ})_{2}\right] \mathrm{Cl}$ | 160.1, 159.0, 158.9, 158.0, 157.5, 157.4, 153.5, 152.9, 151.0, 148.4, 146.8, 146.4, 143.3, $142.9,141.9,132.9,132.4,130.5,129.9,129.6,129.4,129.1,127.7,127.5,126.9,123.7$, 123.4, 120.6. |
| $\left[\mathrm{RhI}_{2}(\mathrm{PQ})_{2}\right] \mathrm{I}$ | $159.5,158.5,157.6,157.2,156.4,156.0,149.9,149.7,148.5,147.8,145.1,143.4,142.6$, $142.4,141.6,136.4,132.3,131.6,130.0,129.8,129.7,129.5,128.4,127.7,126.5,125.1$, 123.9, 119.7. |
| $\left[\mathrm{Rh}\left(\mathrm{N}_{3}\right)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}(\mathrm{PQ})\right] \mathrm{PF}_{6}$ | $\begin{aligned} & 155.8,155.6,149.5,147.5,137.7,137.5,130.3,129.6,128.3,128.2,127.3,125.0,121.5 \text {, } \\ & \text { 118.7. } \end{aligned}$ |

${ }^{(a) 13} \mathrm{C}$ NMR data obtained in DMSO- $\mathrm{d}_{6}$ at 50 MHz . ${ }^{\text {(b) } 13} \mathrm{C}$ NMR data obtained in DMSO- $\mathrm{d}_{6}$ at 100 MHz (see Ref. 14).
${ }^{13} \mathrm{C}$ NMR properties of the PQ ligand and its complexes are listed in Table IV. For the free ligand, and the complex $\left[\mathrm{Rh}\left(\mathrm{N}_{3}\right)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}(\mathrm{PQ})\right] \mathrm{PF}_{6}$, the spectra show fourteen different types of carbon. However, based on steric factors, ${ }^{8}$ structure $\mathbf{E}$ in Figure 2 may be suggested for the $\left[\mathrm{Rh}\left(\mathrm{N}_{3}\right)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}(\mathrm{PQ})\right] \mathrm{PF}_{6}$ complex. The spectra of all other complexes show twenty-eight different types of carbon atoms supporting the structure shown in Figure 3 (equivelant to structure $\mathbf{A}$ in Figure 2). On the other hand, structures $\mathbf{B}$ and $\mathbf{C}$ in Figure 2 should give fourteen different types of carbon. The most deshielded chemical shifts is observed for $\mathrm{C}(2)$ and $\mathrm{C}\left(2^{\prime}\right)$, which are close to the nitrogen atoms of the PQ ligand (Figure 1). In addition, the ${ }^{13} \mathrm{C}$ NMR spectrum of $\left[\mathrm{Rh}(\mathrm{SCN})_{2}(\mathrm{PQ})_{2}\right] \mathrm{Cl}$ shows another signals at 117.5 , and 117.2 ppm , which may be assigned to the non-equivalent carbon atoms of the thiocyanato groups. ${ }^{12,13}$

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## SAŽETAK

## Kompleksi rodija(III) s 2-(2'-piridil)kinolinom. <br> Priprava i spektroskopska obilježja

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Reakcijom $\mathrm{RhCl}_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ i 2-(2'-piridil)kinolina (PQ) u molnom omjeru 1:2 uz dodatak odgovarajuće natrijeve soli priređeni su novi kompleksi rodija(III): cis-[ $\left.\mathrm{RhX}_{2}(\mathrm{PQ})_{2}\right] \mathrm{Y}\left(\mathrm{X}=\mathrm{NO}_{2}^{-}, \mathrm{Y}=\mathrm{PF}_{6}^{-} ; \mathrm{X}=\mathrm{SCN}^{-}\right.$ili $\mathrm{NO}_{3}$, $\left.\mathrm{Y}=\mathrm{Cl}^{-} ; \mathrm{X}=\mathrm{Y}=\mathrm{I}^{-}\right)$i cis-[ $\left.\mathrm{Rh}\left(\mathrm{N}_{3}\right)_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}(\mathrm{PQ})\right] \mathrm{PF}_{6}$. Spojevi su opisani temeljem elementarnih analiza, mjerenja molarne vodljivosti te infracrvene, ${ }^{1} \mathrm{H}$ NMR i ${ }^{13} \mathrm{C}$ NMR spektroskopije.


[^0]:    ${ }^{(a)}$ Molar conductivity for $1 \times 10^{-3} \mathrm{M}$ solutions in DMF at $25{ }^{\circ} \mathrm{C}$. ${ }^{(\mathrm{b})} \mathrm{The}$ calculated and found data of sulfur are 9.61 and $9.59 \%$, respectively.

[^1]:    ${ }^{(a)} v$ : stretching vibration, $\gamma$ : out-of-plane bending vibration, $\delta$ : in-plane bending vibration, $\rho_{\mathrm{w}}$ : wagging vibration. b, broad; m, medium; s, strong; sh, shoulder; vs, very strong; w, weak.
    All complexes show $v(\mathrm{C}-\mathrm{H})$ for the aromatic ring in the region $3075-3060 \mathrm{~cm}^{-1}$.
    ${ }^{(\text {b })}$ Coordinated $\mathrm{NO}_{2}: v\left(-\mathrm{NO}_{2}\right): 1433 \mathrm{~s}, 1422 \mathrm{sh}, 1341 \mathrm{vs}, 1316 \mathrm{~s} ; \gamma(\mathrm{ONO}): 840 \mathrm{~m}, 821 \mathrm{~m} ; \rho_{\mathrm{w}}\left(\mathrm{NO}_{2}\right): 400 \mathrm{~s}, 380 \mathrm{~m} ; v(\mathrm{P}-\mathrm{F}): 844 \mathrm{vs}, \mathrm{b} ; 557 \mathrm{~s}$.
    ${ }^{(c)}$ Coordinated SCN: $v(\mathrm{CN}): 2124 \mathrm{vs} ; v(\mathrm{CS}): 721 \mathrm{~m} ; \delta(\mathrm{NCS}): 468 \mathrm{~m}$.
    ${ }^{(d)}$ Coordinated $\mathrm{NO}_{3}: v\left(-\mathrm{NO}_{2}\right): 1420 \mathrm{~m}, 1335 \mathrm{~m}, 1027 \mathrm{w} ; \gamma(\mathrm{NO}): 1004 \mathrm{w} ; \rho_{\mathrm{w}}\left(\mathrm{NO}_{2}\right): 400 \mathrm{~m}, \mathrm{~b}$.
    ${ }^{(e)}$ Coordinated $\mathrm{N}_{3}: 2125$ vs, 2030 vs; coordinated $\mathrm{H}_{2} \mathrm{O}: v(\mathrm{O}-\mathrm{H}): 3440-3410 \mathrm{~s}, \mathrm{~b} ; \gamma(\mathrm{HOH}): 1625-1610 \mathrm{~m} ; v(\mathrm{P}-\mathrm{F}): 846 \mathrm{vs}, \mathrm{b} ; 556 \mathrm{~s}$.
    ${ }^{(f)} \mathrm{NA}: v(\mathrm{Rh}-\mathrm{I})$ : not seen.

[^2]:    ${ }^{(a)} \mathrm{H}$ NMR data obtained in DMSO- $\mathrm{d}_{6}$ at 200 MHz . d, doublet; 2d, two doublets; dd, doublet of doublet; dt, doublet of triplet; t , triplet; m, multiplet. ${ }^{(b)} \mathrm{H}$ NMR data obtained in DMSO- $\mathrm{d}_{6}$ at 400 MHz (see Ref. 14).

