

# Synthesis and characterization of $[\text{RuCl}_2(\text{picoline})_4]$ complexes: Crystal structure of $[\text{RuCl}_2(\beta\text{-pic})_4]$

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Received 10 February 2005; accepted 18 March 2005

Available online 3 June 2005

## Abstract

The reaction of the  $[\text{RuCl}_2(\text{PPh}_3)_3]$  complex with picolines has been examined. New ruthenium(II) complexes –  $[\text{RuCl}_2(\text{C}_6\text{H}_7\text{N})_4]$  have been obtained and characterized by IR, <sup>1</sup>H NMR and UV–Vis measurements. The crystal structure of the  $[\text{RuCl}_2(\beta\text{-pic})_4]$  complex has been determined. The electronic spectra of the complexes have been calculated by the TDDFT method.

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**Keywords:** Ruthenium; Picoline; X-ray structure; TDDFT method

## 1. Introduction

The five-coordinate ruthenium(II) complex  $[\text{RuCl}_2(\text{PPh}_3)_3]$  is well known as a very useful precursor for the preparation of a wide range of ruthenium compounds, including N-donor derivatives [1–4]. The reactions of the complex with imidazole and N-methylimidazole lead to complexes with tertiary phosphines such as  $[\text{RuCl}_3(\text{PPh}_3)\text{L}_2]$  and  $[\text{RuCl}_2(\text{PPh}_3)_2\text{L}_2]$  (where L = imidazole or methylimidazole) [5]. Triphenylphosphine ruthenium complexes containing other N-donors such as pyridine, bipyridyl, 1,10-phenanthroline are also known [6].

The density functional theory (DFT) is a very popular computational method for the calculation of a number of molecular properties. Because of its greater computational efficiency, DFT has been applied exten-

sively to inorganic and organometallic complexes [7–11]. The time-dependent generalization of DFT (TDDFT) offers a rigorous route to calculate the dynamic response of charge density [12–14]. The reliability of the TDDFT approach in obtaining accurate predictions of excitation energies and oscillator strengths is well documented. The method has been successfully used to calculate the electronic spectra of transition metal complexes with a variety of ligands [15–17].

In this paper, we present the synthesis, spectroscopic properties, electronic structure of new picoline ruthenium(II) complexes and the crystal structure of  $[\text{RuCl}_2(\beta\text{-pic})_4]$ .

## 2. Experimental

All reagents used in the synthesis of the complexes are commercially available and were used without further purification. The  $[\text{RuCl}_2(\text{PPh}_3)_3]$  complex was synthesized according to the literature method [18]. The solvent used in the reaction was argon saturated.

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<sup>1</sup> A holder of the Foundation for Polish Science (FNP) scholarship.

The complexes were prepared by adding the appropriate picoline (0.2 ml) to the solution of  $[\text{RuCl}_2(\text{PPh}_3)_3]$  (0.2 g) in methanol (100 ml). The reaction mixture was stirred for 4 h. The solvent was then removed in vacuo and the crude residue was crystallized from methanol. Crystals of  $[\text{RuCl}_2(\beta\text{-pic})_4]$ , suitable for X-ray analysis, were obtained by slow evaporation of the methanolic solution.

### 2.1. $[\text{RuCl}_2(\alpha\text{-pic})_4]$

Yield 60%. *Anal.* Calc. for  $\text{C}_{24}\text{H}_{28}\text{Cl}_2\text{N}_4\text{Ru}$ : C, 52.94; H, 5.18; N, 10.29. Found: C, 52.42; H, 5.12; N, 5.04%. IR (KBr): 3052 ( $\nu_{\text{CH}}$ ), 2974 ( $\nu_{\text{CH}}$ ), 1604 ( $\nu_{\text{C=N}}$ ), 1481 ( $\nu_{\text{ring}}$ ), 1435 ( $\nu_{\text{C=C}}$ ), 1303 ( $\nu_{\text{ring}}$ ), 1187 ( $\delta_{\text{CH}}$ ), 1093 ( $\delta_{\text{CH}}$ ), 696 ( $\delta_{\text{ring}}$ ), 536 ( $\nu_{\text{M-N}}$ ).  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ): 8.36 (dd H6 pic), 7.23 (t H5 pic), 7.56 (td H4 pic), 7.27 (d H3 pic), 2.59 ( $\text{CH}_3$ ). UV–Vis ( $\text{CH}_2\text{Cl}_2$ ): 645.8 (1.90), 386.0 (3.81), 265.6 (4.74), 228.4 (5.32), 215.8 (5.03).

### 2.2. $[\text{RuCl}_2(\beta\text{-pic})_4]$

Yield 63%. *Anal.* Calc. for  $\text{C}_{24}\text{H}_{28}\text{Cl}_2\text{N}_4\text{Ru}$ : C, 52.94; H, 5.18; N, 10.29. Found: C, 52.72; H, 5.22; N, 5.14%. IR (KBr): 3077 ( $\nu_{\text{CH}}$ ), 3050 ( $\nu_{\text{CH}}$ ), 1615 ( $\nu_{\text{C=N}}$ ), 1484 ( $\nu_{\text{ring}}$ ), 1420 ( $\nu_{\text{C=C}}$ ), 1335 ( $\nu_{\text{ring}}$ ), 1195 ( $\delta_{\text{CH}}$ ), 1051 ( $\delta_{\text{CH}}$ ), 650 ( $\delta_{\text{ring}}$ ), 556 ( $\nu_{\text{M-N}}$ ).  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ): 8.87 (H2 pic), 7.31 (d H4 pic), 7.31 (dd H5 pic), 8.81 (d H6 pic), 2.18 ( $\text{CH}_3$ ). UV–Vis ( $\text{CH}_2\text{Cl}_2$ ): 513.4 (1.92), 427.0 (3.48), 381.8 (3.91), 244.4 (4.20), 222.2 (5.32), 215.8 (5.34).

### 2.3. $[\text{RuCl}_2(\gamma\text{-pic})_4]$

Yield 67%. *Anal.* Calc. for  $\text{C}_{24}\text{H}_{28}\text{Cl}_2\text{N}_4\text{Ru}$ : C, 52.94; H, 5.18; N, 10.29. Found: C, 52.47; H, 5.18; N, 5.12%. IR (KBr): 3049 ( $\nu_{\text{CH}}$ ), 3023 ( $\nu_{\text{CH}}$ ), 1614 ( $\nu_{\text{C=N}}$ ), 1481 ( $\nu_{\text{ring}}$ ), 1432 ( $\nu_{\text{C=C}}$ ), 1385 ( $\nu_{\text{ring}}$ ), 1209 ( $\delta_{\text{CH}}$ ), 1088 ( $\delta_{\text{CH}}$ ), 724 ( $\delta_{\text{ring}}$ ), 531 ( $\nu_{\text{M-N}}$ ).  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ): 8.50 (d H2, H6 pic), 7.25 (d H3, H5 pic), 2.23 ( $\text{CH}_3$ ). UV–Vis ( $\text{CH}_2\text{Cl}_2$ ): 527.1 (1.91), 431.6 (3.77), 352.0 (4.22), 272.6 (4.81), 228.2 (5.21), 214.6 (5.05).

### 2.4. Physical measurements

Infrared spectra were recorded on a Nicolet Magna 560 spectrophotometer in the spectral range 4000–400  $\text{cm}^{-1}$  with the samples in the form of KBr pellets. Electronic spectra were measured on a spectrophotometer Lab Alliance UV–Vis 8500 in the range 800–180 nm in deoxygenated dichloromethane solution. Elemental analyses (C, H, N) were performed on a Perkin–Elmer CHN-2400 analyzer. The  $^1\text{H}$  NMR spectra were recorded on a Bruker DRX-400 spectrometer in  $\text{CDCl}_3$  solutions.

### 2.5. Crystal structure determination and refinement

A rectangular prism crystal was mounted on a KM-4-CCD automatic diffractometer equipped with CCD detector, and used for data collection. X-ray intensity data were collected with graphite monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at a temperature of 293.0(2) K, with the  $\omega$  scan mode. A 12 s exposure time was used and all the Ewald sphere was collected up to  $2\theta = 50.22^\circ$ . The unit cell parameters were determined from least-squares refinement of the setting angles of 5589 strongest reflections. Details concerning crystal data and refinement are given in Table 1. Examination of 98 reflections on two reference frames monitored after each 20 frames measured showed 2.61% loss of the intensity. During the data reduction, the above decay correction coefficient was taken into account. The orange, transparent crystal used for the data collection did not change its appearance. Lorentz, polarization and numerical absorption [19] corrections were applied. The structure was solved by direct methods and subsequently completed by difference Fourier recycling. 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 refined as “riding” on the adjacent carbon atom with an individual isotropic temperature fac-

Table 1  
Crystal data and structure refinement details of  $[\text{RuCl}_2(\beta\text{-pic})_4]$

Empirical formula	$\text{C}_{24}\text{H}_{28}\text{Cl}_2\text{N}_4\text{Ru}$
Formula weight	544.47
Temperature (K)	293(2)
Crystal system	tetragonal
Space group	$P4nc$
<i>Unit cell dimensions</i>	
<i>a</i> ( $\text{\AA}$ )	11.1792(6)
<i>b</i> ( $\text{\AA}$ )	11.1792(6)
<i>c</i> ( $\text{\AA}$ )	10.1596(6)
Volume ( $\text{\AA}^3$ )	1269.69(12)
<i>Z</i>	2
Calculated density ( $\text{Mg/m}^3$ )	1.424
Absorption coefficient ( $\text{mm}^{-1}$ )	0.846
<i>F</i> (000)	556
Crystal dimensions (mm)	0.572 × 0.349 × 0.274
$\theta$ Range for data collection ( $^\circ$ )	3.65–25.11
Index ranges	$-13 \leq h \leq 13$ , $-13 \leq k \leq 13$ , $-12 \leq l \leq 12$
Reflections collected	16 633
Independent reflections [ $R_{\text{int}}$ ]	1133 [0.0373]
Data/restraints/parameters	1133/1/74
Goodness-of-fit on $F^2$	1.119
Final <i>R</i> indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0373$ , $wR_2 = 0.1037$
<i>R</i> indices (all data)	$R_1 = 0.0389$ , $wR_2 = 0.1054$
Largest difference in peak and hole ( $\text{e \AA}^{-3}$ )	0.282 and $-0.297$

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