

Equilibrium and kinetic studies of the reactions between [Ru(terpy)(bipy)Cl]Cl complex and biologically important N-donor ligands

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Дигитални репозиторијум Рударско-геолошког факултета Универзитета у Београду

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Equilibrium and kinetic studies of the reactions between $[\text{Ru}(\text{terpy})(\text{bipy})\text{Cl}]^+$ complex and biologically important N-donor ligands

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Introduction

The studies in the field of anticancer characteristics of ruthenium(III/II) compounds have caused much attention for several years since some of them such as KP1019 (indazolium-tetrachloridobis(H-indazole)ruthenate(III)) i NAMI-A (imidazolium-*trans*-tetrachlorido(dimethylsulfoxide)indazolruthenate(III)) reached the level of clinical investigation.^{1,2}

Experimental

We studied the kinetics of the substitution reactions of $[\text{Ru}(\text{terpy})(\text{bipy})\text{Cl}]^+$ complex with biologically important ligands: dimethylsulfoxide, guanosine-5'-monophosphate, thiourea and L-histidine. All reactions were studied by UV-VIS spectrophotometry in 0.1 M NaClO_4 with 10 mM NaCl. The excess of ligand concentration was used to observed *pseudo*-first order conditions. The rate constants and activation parameters are calculated using computational program Origin 6.1. Also we investigated the hydrolysis and complexation reactions of Ru(II) complex with guanosine-5'-monophosphate and L-histidine. Potentiometric titrations were carried out at 298 K in inert atmosphere using a glass electrode. For the calculations is used computation program HYPERQUAD2006.³

Results

Table 1. Rate constants for the substitution reactions of $[\text{Ru}(\text{terpy})(\text{bipy})\text{Cl}]^+$ complex with nucleophiles in 0.1 mol NaClO_4 and 10 mM NaCl.

ligandi	$[\text{Ru}(\text{terpy})(\text{bipy})\text{Cl}]^+$	
	k_2 [$\text{M}^{-1}\text{s}^{-1}$]	k_1 [s^{-1}]
5'-GMP	$(1.30 \pm 0.03) \times 10^{-4}$	$(2.00 \pm 0.07) \times 10^{-5}$
DMSO	$(1.97 \pm 0.20) \times 10^{-2}$	$(1.23 \pm 0.06) \times 10^{-4}$
Tiourea	$(1.89 \pm 0.07) \times 10^{-1}$	$(1.38 \pm 0.20) \times 10^{-4}$
Histidin	$(4.06 \pm 0.20) \times 10^{-1}$	$(1.14 \pm 0.07) \times 10^{-3}$

Table 2. Stability constants of $[\text{Ru}(\text{terpy})(\text{bipy})\text{H}_2\text{O}]^{2+} - \text{L}$ complexes formed in a 0.1 mol/dm³ NaClO_4 ionic medium, at 298 K.

Species (p,q,r) ^a	$\log \beta_{p,q,r} \pm \sigma$		
		5'-GMP	His
(1, -1, 0)	-7.12(4)		
(2, -1, 0)	-1.34(4)		
(1, 0, 1)			5.06(9)
(1, 1, 1)		14.12(2)	
(2, 1, 1)		18.26(4)	16.51(7)
Statistics	$\chi^2 = 13.32$ $s = 1.96$	$\chi^2 = 12.99$ $s = 1.51$	$\chi^2 = 14.79$ $s = 2.73$

^ap, q and r are the stoichiometric coefficients corresponding to $[\text{Ru}(\text{terpy})(\text{bipy})\text{H}_2\text{O}]^{2+}$, H^+ and ligand, respectively

Conclusion

- The reactivity of the used ligands toward monofunctional $[\text{Ru}(\text{terpy})(\text{bipy})\text{Cl}]^+$ complexes decrease in order: Thiourea>DMSO>His > 5'-GMP.
- As can be seen from Fig. 3, the dominating hydrolytic complex at lower pH values is (2, -1), with maximum a concentration at pH = 7. The formation of the complex (1, -1) starts at about pH=7 and with increasing pH, the concentration of this complex increases.

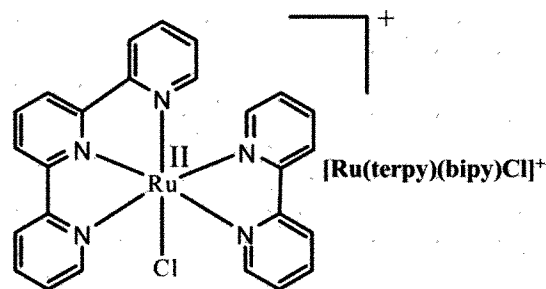


Figure 1. Structures of the investigated complexes

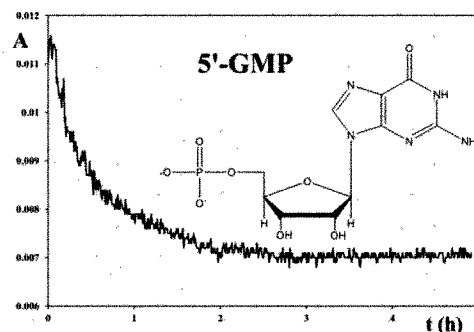


Figure 2. Kinetic traces of the reaction between $[\text{Ru}(\text{terpy})(\text{bipy})\text{Cl}]^+$ ($2 \cdot 10^{-4}$ M) complex and 5'-GMP ($3.3 \cdot 10^{-3}$ M), $T = 310$ K, $\lambda = 380$ nm

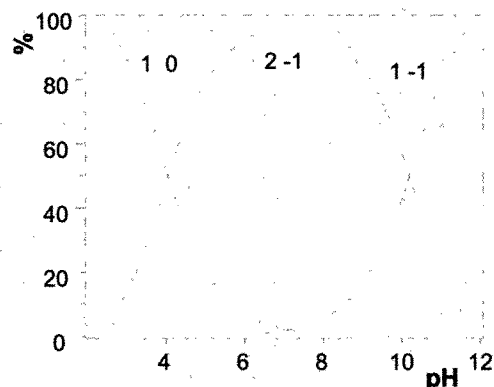


Figure 3. The distribution of $[\text{Ru}(\text{terpy})(\text{bipy})\text{H}_2\text{O}]^{2+}$ hydrolytic species in 0.1 mol dm^{-3} NaClO_4 ionic medium at 298 K.

$C_{[\text{Ru}(\text{terpy})(\text{bipy})\text{H}_2\text{O}]^{2+}} = 2.00$ mmol dm^{-3}

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