XXI Brazilian Meeting on Inorganic Chemistry
X Brazilian Meeting on Rare Earths
III Workshop on Theoretical Bioinorganic Chemistry
Belo Horizonte, September 12 - 15th 2024

Influence of diimine ligand in the ruthenium (II) terpyridine complexes on the kinetics aquation and DNA interaction

Evelyn C. S. Arantes [1] , Allyson L. R. dos Santos[2], Anizio M. de Faria[1,2], Letícia S. Amorim[3], Vinicius S. P. Nunes[3], Diego F. S. Paschoal[3] and Renata G. de Lima[1,2]

[1]*Instituto de Química, Universidade Federal de Uberlândia, Uberlândia/MG, Brazil*
[2] *ICENP, Universidade Federal de Uberlândia, Ituiutaba/MG, Brazil*
[3]*Centro Multidisciplinar UFRJ-Macaé, Universidade Federal do Rio de Janeiro, Macaé/RJ, Brazil*
E-mail: evelyn.arantes@ufu.br

Thematic Area: Biological Inorganic Chemistry

Keywords: terpyridine ruthenium (II) complex, aquation kinetics, DNA interaction

Currently, the exploration and structural understanding of polypyridine ruthenium(II) complexes have evolved due to their promising importance in biological applications[1]. In this work, two complexes of the type $[Ru^{II}Cl(bd)(tpy)]PF_6$ (1) and $[Ru^{II}Cl(bdq)(tpy)]PF_6$ (2), where bd = *o*-phenylenediamine, bdq = 3,4-diaminobenzoic acid and tpy = 2,2';6',2"-terpyridine were synthesized, characterized and evaluate the spontaneous kinetics of the chloride ligand in aqueous solution as well as DNA interaction. In addition, quantum mechanical calculations and molecular docking simulations were also carried out for predicting the structure and kinetics data. The aqua species ($Ru^{II}(H_2O)(tpy)(L)]^{2+}$) formations were accompanied by HPLC technic and the aquation kinetics constants value obtained by UV-visible behavior in aqueous and PBS medium. The aquation kinetics constant are described in the Table 1. The complex 2 demonstrated about 2 times greater labilization kinetics of chloride ligand than complex 1, the same trend was observed in calculations performed at the B97-3c/CPCM level (ORCA 5.0.4 program). The chromatogram for complex (1) shows one peak (t_r = 13 min.) while for the complex (2), 2 peaks with different retention times (t_{r1}=3 and t_{r2}= 4 min.) were founded. The spectral profiles for the two peaks are similar (λ_{max}=506 nm) indicative of the position isomers dependently of the −COOH substituent[2]. Over time, these peaks decrease and the aquo species are formed with others retention time. The interaction with fish sperm DNA (*fs*-DNA) were studied using ethidium bromide replacement (K_{SV} and K_{app}) (Table 1). The chloride species coordinated to bd ligand present a higher interaction by intercalation with *fs*-DNA than the complexes with bdq ligand.

Table 1. Values of water rate constant (experimental and theoretical), half-life time and interaction constant with DNA for complexes 1 and 2. All values were obtained in replicates.

Complex	**k_{aq} (10^{-4} s^{-1})**	**$t_{1/2}$ (min.)**	**k^{cal} (10^{-4} s^{-1})**	**K_{SV} (10^4 L mol^{-1})**		**K_{app} (10^6 L mol^{-1})**	
				chloride	**aquo**	**chloride**	**aquo**
1	**H_2O** 7.04 ± 0.58 **PBS** 1.21 ± 0.25	16 98	1.28	3.58 ± 0.27	4.01 ± 0.35	2.39 ± 0.11	3.06 ± 0.28
2	**H_2O** 14.4 ± 0.28 **PBS** 6.84 ± 0.88	8 17	2.89	2.20 ± 0.22	1.88 ± 0.06	1.33 ± 0.33	1.64 ± 0.03

Acknowledgments: CAPES for master scholarship, RELAM-UFU, and FAPERJ.

References

[1] M. Mital, Z. Ziora. Coordination Chemistry Reviews, **375**, 434, 2018.
[2] A. Oliveira, *et al*. Inorganic Chemistry Communications, **12**, 343, 2009.