

Kinetic Study of the Hydroxide Ion Attack on and DNA Interaction with High Spin Iron(II) Schiff Base Amino Acid Chelates Bearing ONO Donors¹

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Abstract—Kinetic study of some novel high spin Fe(II) complexes of Schiff base ligands derived from 5-bromosalicylaldehyde and amino acids with the OH⁻ ion and DNA has been carried out. Based on the kinetic data, the rate law and a plausible mechanism were proposed. Kinetic data of the base catalyzed hydrolysis imply pseudo first-order double stage process due to the presence of mer- and fac-isomers. The observed rate constants k_{obs} were correlated with the effect of a substituent R in the structure of ligands. The rate constants and activation parameters are in good agreement with stability constants of the studied complexes. Reactivity of the complexes towards DNA correlated well with the reported binding constants.

Keywords: base catalyzed hydrolysis, reactivity, reaction mechanism, thermodynamic parameters, DNA interaction

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INTRODUCTION

The modern strategy for drugs design is based not entirely on the structure but also the mode of action of a drug towards its specific targets. Schiff base complexes are of high importance as radiotracers [1], biologically active reagents [2–5], catalysts of oxidation [6, 7], epoxidation [8], polymerization [9], and decomposition [10, 11] reactions. Over recent decades considerable attention was paid to a variety of low-spin tris-ligand Fe(II) complexes [12–18]. Influence of substituents on basic hydrolysis of tris-ligand-Fe(II) complexes of Schiff base ligands derived from 2-acetylpyridine and substituted benzylamines and their aniline analogues is presented in the publication [19]. Iron(II) Schiff base complexes provide useful structural and electronic models for the similarly coordinated sites detected in heme iron enzymes. Such complexes are important for the asymmetric oxidation of organic substrates as their structure and catalytic activity are similar to those of iron porphyrins [20]. The present study is devoted to

the hydroxide group attack on some newly produced Schiff base amino acid Fe(II) complexes [21] (Scheme 1).

EXPERIMENTAL

Materials and methods for the base hydrolysis reaction. Iron(II) complexes were synthesized according to the method presented in publications [5, 21, 22]. An aqueous solution of an α -amino acid was mixed with hot solution of an aldehyde in ethanol. The resulting Schiff base amino acid ligand was stabilized by chelation with Fe(II) by adding an equivalent quantity of aqueous solution of ferrous ammonium sulfate. For avoiding Fe(II) oxidation 5–6 drops of glacial acetic acid were added. The resulting solution was stirred for 9 h under nitrogen. The isolated complexes were recrystallized from water–ethanol solutions. Compositions of the complexes were elucidated by CHN microanalysis, IR, and UV-Vis spectroscopy, and magnetic moments measurements [5]. Purity of the synthesized complexes was detected spectrophotometrically (Table 1). Stability of Fe(II) cation was tested by its resistance to reduction by dithionite. An aged complex solution was treated with NaOH under N₂ and the following formation of green

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