Experimental and theoretical studies of the substitution reactions of some bifunctional Au(III) complexes with biologically relevant thiols and thioethers

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Abstract

The kinetic of the substitution reactions between bifunctional Au(III) complexes, $[AuCl_2(bipy)]^+$, $[AuCl_2(dach)]^+$ and $[AuCl_2(en)]^+$ (bipy = 2.2'-bipyridine, dach = (1R,2R)-1,2-diaminocyclohexane, en = ethilendiamine) with biologically relevant ligands such as: glutathione (GSH), L-methionine (L-Met) and L-cysteine (L-Cys) is determined. All kinetic studies are performed in 25 mM Hepes buffer (pH = 7.2) in the presence of NaCl (25 mM) to prevent the hydrolysis of the complexes. The reactions were followed under the *pseudo*-first order conditions, using stopped-flow UV-Vis spectrophotometry at before determined working wavelenghts, at three different temperatures (288.2, 298.1 and 309.8 K). DFT theoretical approach was applied to calculate thermodynamic and kinetic parameters that determined an operative mechanism of substitution reactions for all estimated complexes, and for L-Cys as a selected model of substituent. The obtained kinetic data showed that all complexes have similar reactivity, the $[AuCl_2(bipy)]^+$ complex is the most reactive while the $[AuCl_2(en)]^+$ complex is the least reactive. The second step of the substitution reaction is much faster than the first. The reactivity of the studied nucleophiles decreases in order: L-Met > L-Cys >GSH. According to the values of the activation parameters determined experimentally and theoretically, all substitutions follow an associative model.

Keywords: Gold(III), complexes, kinetics, thermodynamics, substitution, DFT

Graphical Abstract