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ORIGINAL PAPER

Kinetics of chloride substitution in $[Pt(bpma)Cl]^+$ and [Pt(gly-met-*S*,*N*,*N*)Cl] complexes by thiourea, nitrites, and iodides

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Substitution of chloride in $[PtCl(bpma)]^+$ and [PtCl(gly-met-*S*,*N*,*N*)], where bpma is bis(2-pyridylmethyl)amine and gly-met-*S*,*N*,*N* is glycyl-L-methionine, was studied as a function of the entering nucleophile concentration and temperature. Reactions between the platinum(II) complexes and thiourea (TU), iodides (I^-), and nitrites(III) (NO_2^-) were carried out in aqueous solutions using conventional UV-VIS spectrophotometry. Suitable ionic conditions were reached by an addition of 0.1 M $NaClO_4$ and 0.01 M NaCl (to suppress hydrolysis). The second-order rate constants, k_2, for the studied reactions with NO_2^- varied between 0.036–0.038 M^{-1} s^{-1}, and for the reactions with TU between 0.095–1.06 M^{-1} s^{-1}, respectively. The reaction between TU and the $[PtCl(bpma)]^+$ ion is ten times faster than that of the [PtCl(gly-met-*S*,*N*,*N*)] complex. An analysis of the activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, for the selected reactions clearly shows their associative nature.

Keywords: platinum(II) complexes, substitution, kinetics, thiourea, nitrites(III), iodides

Introduction

Platinum(II) complexes are characterized by two important features: inert substitution reactions and nontrivial antitumour properties (Lippert, 1999; Tobe & Burgess, 1999). The combination of these two aspects makes the complexes very suitable as well as significant objects for kinetic studies.

The complexes selected for the present work possess only one ligand, chloride, able to be substituted in solution. Thus, kinetics of the studied reactions can be described by a relatively simple model without additional complications resulting from the second step of the reaction. Thus, these complexes represent good models for mechanistic and kinetic studies of the reactions of platinum(II) anticancer drugs with *S*- and *N*-donor ligands (Bogojeski & Bugarčić, 2011). Among the ligands coordinating the platinum(II) centers described in this paper, bis(2-pyridylmethyl)amine (bpma) is the most presented in literature (Pitteri et al., 2001, 2002; Nagy et al., 2003; Guney et al., 2011) due to many factors such as: *i*) location of pyridine rings in the coordination plane favoring possible interactions of the π systems of metal and ligand (Jaganyi, 2001; Pitteri et al., 2001), and *ii*) relatively simple structure connected with strong coordination ('chelate effect') (Nagy et al., 2003). Considering the kind of the donor atom of incoming ligands, a lot of papers focus on the *N*- and *S*-donor nucleophiles (Bugarčić et al., 2004a, 2004b, 2012; Summa et al., 2006; Bogojeski et al., 2010; Hochreuther et al., 2011; Petrović et al., 2012; Ruhayel et al., 2012). To extend the scope of the studied nucleophiles, reaction studies of the chosen platinum(II) complexes (Fig. 1) and I^-, TU, and NO_2^- have been done and are presented below. Although neither of the studied complexes is important due to its antitumour activity (Bogojeski & Bugarčić, 2011), the reactions studied in this paper bring some new information about the substitution in $[PtCl(bpma)]^+$ and [PtCl(gly-met-*S*,*N*,*N*)], which can be useful in the overall interpretation of kinetic data collected for these complexes (Bugarčić et al., 2007;

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