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Kinetics and mechanism of Pt(II)-sulfur adduct formation with bio-relevant molecules *in vitro* aqueous medium: Their anticancer activity, DNA binding, drug reservoir property and a theoretical approach

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Synthesis and cytotoxic property of Pt(II)-sulfur adducts are significant in biological aspect. In order to investigate their relevance, two Pt(II) model complexes were considered for detailed study. *In-vitro* kinetics and their mechanism, drug reservoir property of the complexes [Pt(ambim)(H2O)2]X2 1A, [Pt(MAMP)(H2O)2]X2 2A (where, AMBIM= 2-aminomethylbenzimidazole, MAMP = 2-[(N-methylamino)methyl]pyridine and X= NO3- or ClO4-) with sulfur containing bio-molecules DL-methionine (DL-meth), DL-penicillamine (DL-pen) and Glutathione (GSH) were studied to explore the 'drug reservoir' mechanism. The complexes [Pt(ambim)(DL-pen)] 1B, [Pt(ambim)(GSH)] 1C, [Pt(MAMP)(DL-meth)] 2B and [Pt(MAMP)(DL-pen)] 2C were synthesized from complexes 1A and 2A, which was obtained from the hydrolysis of complexes [Pt(ambim)Cl2] and [Pt(MAMP)Cl2] and characterized by spectroscopic methods. Interaction mechanism between the diaqua complexes with S-containing ligands have been established by kinetic study. Two step consecutive reaction rate constants (k1 and k2) and corresponding activation parameters (ΔH and ΔS) for both the steps were calculated and an associative mechanism was proposed. Theoretical investigations like structural optimization, HOMO-LUMO energy calculations, NBO analysis were performed to get an insight into their electronic structure. The coordination mode of the biomolecules via (S, O) were established by spectroscopic methods and confirmed by NBO analysis. DNA binding property of the complexes 2-4 were investigated by UV-Vis spectra, competitive binding experiment, gel electrophoresis and their corresponding binding constants (kb and ksv) were calculated. The computational molecular docking study was carried out for the complexes with B-DNA to confirm their DNA binding mode. Cytotoxic property of the proposed complexes were investigated on HeLa, HepG2 and A549 cell lines. Their corresponding IC50 values were calculated and compared with the well known anticancer drug cisplatin.

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