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Kinetics and mechanistic study of polynuclear platinum(II) polypyridyl complexes; A paradigm shift in search of new anticancer agents

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Abstract	<p>This paper reports on a mechanistic interaction between mononuclear and polynuclear platinum(II) complexes <i>viz</i>: phenyl-dichlorido-2,2'-dipyridinylaminediaquaplatinum(II) (PtC1); di-2-pyridylaminomethylbenzenediaquaplatinum(II) (PtC2); 1,3,5-tris(2,2'-dipyridylamino)-benzenehexaquaplatinum(II) (PtC3); 1,3,5-tris(2,2'-dipyridylmethylamino)benzenehexaquaplatinum(II) (PtC4); and 2,4,6-tris(2,2'-dipyridylamino)-1,3,5-triazinehexaquaplatinum(II) (PtC5) with thiourea nucleophiles under <i>pseudo</i>-first-order conditions as a function of nucleophile concentration and temperature using stopped-flow and UV-Vis spectrophotometric techniques. The reactivity of the complexes followed the order PtC5 > PtC1 > PtC3 > PtC2 > PtC4 with thiourea (TU) as the entering nucleophile. The study demonstrates that both rigidity and flexibility has an influence on the kinetics of the complexes and governs by both steric and electronic effects. Introduction of methylene groups destroys conjugacy and lowers the acidity of the complexes. Kinetic and DFT data concur and illustrates that electron donation by methylene bridge leads to stabilization of the complexes. The study further shows that replacement of the methyne (=CH-) groups with nitrogen atoms enhances reactivity. The small positive enthalpy of activation and large negative values of entropy of activation indicate an associative mode of activation for aqua ligand substitutions and dechelation processes.</p>

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