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#### Research paper

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

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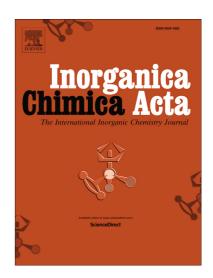
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# ACCEPTED MANUSCRIPT

Full Title	Kinetics and mechanistic study of polynuclear platinum(II)
	polypyridyl complexes; A paradigm shift in search of new anticancer agents
Article type	Research paper
Keywords:	Reactivity, rigidity, flexibility, methylene, associative
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Abstract	This paper reports on a mechanistic interaction between mononuclear
	and polynuclear platinum(II) complexes viz; phenyl-dichlorido-2,2'-
	dipyridinylaminediaquaplatinum(II) (PtC1); di-2-
	pyridylaminomethylbenzenediaquaplatinum(II) (PtC2); 1,3,5-
	tris(2,2'dipyridylamino)-benzenehexaquaplatinum(II) ( <b>PtC3</b> ); 1,3,5-
	tris(2,2'dipyridylmethylamino)benzenehexaquaplatinum(II) ( <b>PtC4</b> );
	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.

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