UGC Major Research Project

Title of the Project: Synthesis, characterization, spectral and catalytic studies of transition metal complexes of some biologically important aroylhydrazone ligands

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Summary

Ru(II) complexes with tridentate ligands viz. (4-hydroxy-N’-(pyridin-2-yl-ethylene) benzohydrazide [Ru(L\textsuperscript{1})(PPh\textsubscript{3})\textsubscript{2}(Cl)] (1), N’-(pyridin-2-yl-methylene) nicotino hydrazide [Ru(L\textsuperscript{2})(PPh\textsubscript{3})\textsubscript{2}(Cl)] (2), N’-(1H-imidazol-2-yl-methylene)-4-hydroxybenzohydrazide [Ru(L\textsuperscript{3})(PPh\textsubscript{3})\textsubscript{2}(Cl)] (3) and N’-(1H-imidazol-2-yl-methylene) nicotino hydrazide [Ru(L\textsuperscript{4})(PPh\textsubscript{3})\textsubscript{2}(Cl)] (4) have been synthesized and characterized. Single crystal structures of acetonitrile coordinated ruthenium complexes of 1 and 3 [Ru(L\textsuperscript{1})(PPh\textsubscript{3})\textsubscript{2}(CH\textsubscript{3}CN)]Cl (1a) and [Ru(L\textsuperscript{3})(PPh\textsubscript{3})\textsubscript{2}(CH\textsubscript{3}CN)]Cl (3a) revealed tridentate ligands with significantly distorted octahedral geometry constructed by imine nitrogen, heterocyclic nitrogen and enolate amide oxygen, forming a cis-planar ring with trans-placement of two PPh\textsubscript{3} groups and a coordinated acetonitrile. Ligands (L\textsuperscript{1H}-L\textsuperscript{4H}) and their ruthenium complexes are characterized by \textsuperscript{1}H, \textsuperscript{13}C, \textsuperscript{31}P NMR and IR spectral analysis. Ru(II) complexes have reversible to quasi-reversible redox behavior with Ru(II)/Ru(III) oxidation potential of 0.40 – 0.71 V. The DNA binding constants determined by absorption spectral titrations with Herring Sperm DNA (HS-DNA) reveal that L\textsuperscript{4H} and 1 interact more strongly than other ligands and Ru(II) complexes. DNA binding studies also suggest that aroylhydrazone ligands bind through strong electrostatic attractions due to presence of heterocyclic ring while their complexes exhibit hyper and hypo-chromic shifts suggesting their binding affinity towards both minor and major grooves. Interaction of ligands with plasmid DNA leads to increase in nicked circular form as well as cleaving of double strands, thereby generating linear strands. Such behavior is also observed for the complexes with 1 exhibiting better interaction probably due to the reversible Ru(II)/Ru(III)couple. Presence of two heterocyclic rings within the ligand structure account for such behavior. Complexes 1-3 exhibit DNA cleaving activity possibly due to strong electrostatic interactions while 4 displays intercalation.

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