

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(L¹)(PPh₃)₂(Cl)] (1), N'-(pyridin-2-yl-methylene) nicotinohydrazide [Ru(L²)(PPh₃)₂(Cl)] (2), N'-(1H-imidazol-2-yl-methylene)-4-hydroxybenzohydrazide [Ru(L³)(PPh₃)₂(Cl)] (3) and N'-(1H-imidazol-2-yl-methylene) nicotinohydrazide [Ru(L⁴)(PPh₃)₂(Cl)] (4) have been synthesized and characterized. Single crystal structures of acetonitrile coordinated ruthenium complexes of 1 and 3 [Ru(L¹)(PPh₃)₂(CH₃CN)]Cl (1a) and [Ru(L³)(PPh₃)₂(CH₃CN)]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 PPh₃ groups and a coordinated acetonitrile. Ligands (L¹H-L⁴H) and their ruthenium complexes are characterized by ¹H, ¹³C, ³¹P 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 L⁴H 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.

Publication out of this project:

- a) Ruthenium(II) complexes of aroylhydrazones: Structural, electrochemical and electrostatic interactions with DNA, *Journal of Coordination Chemistry*, 2017 (in press).

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