

ABSTRACT**Synthesis, Characterization, and Molecular Sensing Behaviour of a Variety of Di-2-pyridyl Ketone Hydrazone Derivatives****Orville Charles Anthony Green**

This research is in continuation of previously reported studies on the development of di-2-pyridyl ketone derivatives and aims to improve the molecular sensing capabilities and to understand the factors that influence the behavior of these systems.

A series of di-2-pyridyl ketone (dpk) derivatives, dpkabh.H₂O, dpktch, dpknph, dpkbh and their metal compounds were synthesized and characterized using a number of spectroscopic methods. The free ligands (dpk-derivatives) were synthesized from the reaction of dpk with the targeted hydrazine or hydrazide compounds in refluxing acidified alcohol. The metal compounds of dpk or dpk-derivatives were prepared from the reaction of the appropriate inorganic starting material with the selected dpk or dpk-derivative in non-aqueous solvent under ultrasonic radiation or refluxing conditions.

Spectroscopic measurements revealed sensitivity of dpk-hydrazone derivatives to changes in their surroundings. The electronic absorption spectra of dpk-hydrazone derivatives and their metal compounds is dominated by two intra-ligand charge transfer (ILCT) transitions that may be due to $\pi-\pi^*$ of dpk followed by dpk to hydrazone charge transfer. Spectrophotometric measurements in protophilic solvents show dpk-hydrazone and their metal compounds to be able to

detect and determine low concentrations of substrates, for example, group 12 metal ions, NaBH_4 , KPF_6 and glucose. $^1\text{H-NMR}$ studies done on $\text{dpkabh}\cdot\text{H}_2\text{O}$ and $[\text{ZnCl}_2(\eta^3\text{-N,N,O-dpkbh})]$ show sensitivity of the amide proton of the hydrazone backbone to changes in its surrounding. Electrochemical measurements in non-aqueous media done on *fac*- $[\text{Mn}(\text{CO})_3(\eta^2\text{-N,N-dpk})\text{Br}]$ show rich electrochemical properties and sensitivity of the redox processes to changes in their environment. X-ray structural analysis was used to elucidate the structure of the isolated compounds.

Keywords: Di-2-pyridyl ketone; Hydrazones; Sensors; Synthesis; Rhenium; Zinc; Manganese; Mercury; Molybdenum; Spectroscopy; Electrochemistry; Metal complexes; X-ray crystallography.