ABSTRACT

Monosubstituted Squarate Ligands and Their Transition Metal and Lanthanide Complexes:
Structural and Electrochemical Studies

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Complexation of the monosubstituted squarate ligands (methylsquarate, phenylsquarate and diphenylaminosquarate) with first row transition (Mn, Co, Ni, Zn) and lanthanide (Gd, Tb) metals resulted in the production of neutral polymers: $\{M[\mu\text{-}(C_6H_5)_2NC_4O_3][(C_6H_5)_2C_4O_3][H_2O]_3\}_n$ (M = Co, Zn); $\{Mn[\mu\text{-}(C_6H_5)_2NC_4O_3]_2[H_2O]_4\}_n$; $M[\mu\text{-}(C_6H_5C_4O_3)][(C_6H_5C_4O_3)_2(H_2O)_4]$ (M = Gd, Tb); ionic polymers: $\{M[\mu\text{-}(CH_3C_4O_3)_2][(H_2O)_4][NO_3]\cdot H_2O\}_n$ (M = Gd, Tb); a monomer: $[Ni(C_6H_5C_4O_3)_2(H_2O)_4]$; and a salt: $[Ni(H_2O)_6][(C_6H_5)_2NC_4O_3]_2\cdot 2H_2O$. Electrochemical studies of the methylsquarate, phenylsquarate and diphenylaminosquarate ligands in aqueous solutions using a platinum disk electrode displayed their ability to accept/donate electrons. In addition to this electroactivity, results of the experiments in which the ligands were utilised as mediators in the glucose oxidase/glucose system indicated their ability to serve as electron transfer agents. The electrochemistry of the cobalt, manganese and nickel polymeric complexes revealed oxidation/reduction processes attributable to the ligands as well as to changes in oxidation states of the metal atoms. Solvent dependent electrochemical studies show that the higher oxidation states of the central metal ions in the polymeric complexes were stabilised in aprotic media [*N,N*-dimethylformamide (DMF), dimethylsulphoxide (DMSO)] as opposed to aqueous medium in which dissociation of the complexes occurred.

Keywords: Avril Rae Williams-Dottin; monosubstituted squarate ligands; transition metal and lanthanide complexes; electrochemistry; DMF; DMSO; glucose oxidase/glucose; mediator.