ABSTRACT

SYNTHESES, SPECTRAL AND REDOX PROPERTIES OF SOME RUTHENIUM (II) AND COBALT (III) COMPLEXES CONTAINING ANTRAQUINONE LIGANDS

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The syntheses and properties of $[RuL(bpy)_2]^+$, $[Ru_2L(bpy)_4]^{2+}$ and $[Co_2L(bpy)_4]^{n+}$ where n = 4 - 6, L = a disubstituted anthraquinone ligand and bpy is 2,2'-bipyridine are described. Absorption spectra were analysed and bands (220 - 290 nm) in the ultraviolet region were assigned to ligand $\pi \rightarrow \pi^*$ transitions and visible bands (320 - 550 nm) were assigned to $d\pi \rightarrow \pi^*$ MLCT transitions. The $[Ru_2(1,4\text{-DAAQ})(bpy)_4](PF_6)_4$ and $[Ru_2(1,4\text{-DHAQ})(bpy)_4](PF_6)_2$ complexes were found to exhibit positive solvatochromism in solvent of increasing polarity. The E* MLCT parameter [105] correlated with the MLCT energies of the $[Ru_2(1,4\text{-DHAQ})(bpy)_4](PF_6)_2$ and $[Ru_2(1,4\text{-DAAQ})(bpy)_4](PF_6)_4$ complexes. Slopes of -0.00066 and -0.00088 with correlation coefficients of 0.855 and 0.936 respectively were obtained. The pks of the

mononuclear ruthenium (II) dihydroxyanthraquinone complexes $[Ru(1,8\text{-}DHAQ)(bpy)_2]^+$, $[Ru(1,5\text{-}DHAQ)(bpy)_2]^+$ and $[Ru(1,4\text{-}DHAQ)(bpy)_2]^+$ were determined spectrophotometrically in 90% aqueous solution and found to be 10.77, 10.51 and 10.09 respectively.

Reduction potentials for the $Ru^{3+/2+}$ couples varied from about 0.05 to 0.73 Vs SCE. Two peaks were observed for the binuclear complexes and one for the mononuclear complexes. Three ligand reductions were observed and assigned to the one-electron reduction of each bidentate ligand, commencing with the anthraquinone ligand and then followed by bpy. Reduction potentials for the $Ru^{3+/2+}$ couples and for the first ligand - based reduction were found to correlate in a linear manner. In addition, a linear plot was obtained for the $Ru^{3+/2+}$ couple and the pka of the bound ligand of the mononuclear ruthenium complexes. The influence of the anthraquinone ligands on the $d\pi$ orbitals of ruthenium (II) complexes can be attributed to a combination of σ and π effects. Reduction potential for the $Co^{3+/2+}$ couples varied from +0.28 to -0.26V vs SCE. Ligand reductions were in general not clearly defined. From a study of the effect of changing the ligating atom from oxygen to nitrogen on the anthraquinone ligand it can be concluded that such a change in general leads to more facile reduction of the metal centers. In

addition by comparison with the 1,4-DHAQ and 1,4-DAAQ complexes the $E_{\frac{1}{2}}$ (1) values for the 1,4-AHAQ complexes may be assigned as the reduction of the metal-nitrogen sites.

The self exchange rate constant k11, for the $[Ru_2(1,4\text{-DHAQ})(bpy)_4]^{2+}$, $[Ru_2(1,5\text{-DHAQ})(bpy)_4]^{2+}$ and $[Ru_2(1,4\text{-AHAQ})(bpy)_4]^{3+}$ complexes were estimated to be in the range 10^8 - 10^9 mol^{-1} dm^3 sec^{-1} in acetonitrile at 25°C.