

Diastereoisomeric homo- and heterobimetallic Ru and Os complexes: Manifestation of properties due to electron and proton transfers

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Intramolecular electronic communication in bi- and polynuclear ruthenium(II) and osmium(II) complexes with appropriate bridging and terminal oligopyridine ligands have received considerable attention. However, stereoisomeric complexity of such systems due to the chirality of each *tris*-chelate unit complicates the issue. We report here a series of Ru^{II}Ru^{II}, Os^{II}Os^{II}, and Ru^{II}Os^{II} complexes based on pyrazole-3,5-*bis*(benzimidazole) as the bridging ligand and 2,2'-bipyridine or 1,10-phenanthroline as the terminal ligand. For each complex, either the *meso* ($\wedge\Delta$) and *rac* ($\wedge\wedge$, $\Delta\Delta$) forms or the two enantiomeric pairs ($\wedge\Delta$, $\Delta\wedge$) and ($\wedge\wedge$, $\Delta\Delta$) have been isolated and characterized by NMR spectroscopy and X-ray crystallography. Since these complexes contain dissociable NH protons, physico-chemical studies involving symbiotic electron and proton transfers have been carried out. The remarkable influence of protons on the extent of metal-metal interaction has been observed in terms of profound shifts of redox potentials, metal-to-ligand charge transfer and intervalence transfer transition energies and also the on/off effect of spectral emission.