

Abstract/Synopsis

Mixed valency in a ligand bridged symmetric polynuclear set up arises when the metal centers exist in their different oxidation states. The intermetallic electron and charge-transfer aspects in such molecular frameworks have significance in understanding the electron transfer kinetics in biological processes involving redox-active metalloproteins as well as in developing molecular electronics and optical devices. The extent of intermetallic electronic coupling in the mixed valent state(s) of polynuclear complexes varies primarily depending on the electronic nature of bridging and ancillary ligands as well as on the specific oxidation states of the metal ions. On the other hand, the use of redox active (redox non-innocent) bridging ligands in the complex frameworks creates ambiguities towards the assignment of valence and spin configurations of such complexes as both the metal and ligand centers can take part in electron transfer processes because of closeness of their frontier orbitals. In consequence precise determination of valence and spin situations in transition metal complexes comprising of redox non-innocent ligands is considered to be a formidable challenge. However, further complicacy develops when asymmetry is imposed on such systems through systematic synthetic strategies. In this context, the research work in the thesis has primarily been focused on the synthesis of symmetrical and asymmetrical diruthenium complexes encompassing redox non-innocent bridging ligands. To understand the valence and spin distribution processes in symmetrical dinuclear system, the following complexes $[(\text{acac})_2\text{Ru}(\mu\text{-BL}_1)\text{Ru}(\text{acac})_2]^n$ (acac: 2,4-pentanedionato; BL_1 : 1,2,4,5-tetraimino-3,6-diketocyclohexane) and $[(\text{acac})_2\text{Ru}(\mu\text{-BL}_2)\text{Ru}(\text{acac})_2]^n$ (BL_2 : 2,5-pyrazine-dicarboxylato) have been synthesized. The extent of bridge mediated metal-metal coupling at the mixed valent $\{\text{Ru}^{\text{II}}(\mu\text{-BL})\text{Ru}^{\text{III}}\}$ state has been established by electrochemistry, spectroelectrochemistry (UV-vis-NIR-IR and EPR) and finally by theoretical calculations (DFT). The specific effect of σ -donating ancillary ligand, acac on the electronic structural aspects of the molecules has been scrutinized. On the other hand, to understand the electronic structural aspects of asymmetrical diruthenium complexes, the following molecular frameworks have been synthesized: $[(\text{acac})_2\text{Ru}(\mu\text{-BL}_3)\text{Ru}(\text{bpy})_2]^n$ and $[(\text{acac})_2\text{Ru}(\mu\text{-BL}_3)\text{Ru}(\text{Cym})\text{Cl}]^n$ (BL_3 : 2,2'-azobispyridine, bpy: 2,2'-bipyridine or Cym: *p*-cymene). The valence and spin situations of the complexes in the accessible redox states have been authenticated by various experimental techniques and theoretical calculations. Finally, redox non-innocent behavior of the *modified* β -diketonato system (9-oxidophenalenone = L^-) has been established in the molecular frameworks of $[\text{Ru}(\text{L}^-)(\text{bpy})_2]^k$, $[\text{Ru}(\text{L}^-)_2(\text{bpy})]^m$, and $[\text{Ru}(\text{L}^-)_3]^n$ via detailed experimental and theoretical calculation.