

A Five-Center Redox System: Molecular Coupling of Two Non-Innocent Imino-*o*-benzoquinato-Ruthenium Functions through a π Acceptor Bridge

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Combining the concepts of non-innocent behavior of metal/ligand entities and the coupling of redox-active moieties via an electronically mediating bridge led to the synthesis, the structural, electrochemical and spectroscopic characterization of $[\text{Cl}(\text{Q})\text{Ru}(\mu\text{-tppz})\text{Ru}(\text{Q})\text{Cl}]^n$ where Q^0 is 4,6-di-*tert*-butyl-*N*-phenyl-*o*-iminobenzoquinone and tppz⁰ is 2,3,5,6-tetrakis(2-pyridyl)pyrazine, the available oxidation states being $\text{Ru}^{\text{II,III,IV}}$, $\text{Q}^{0,-2-}$ and tppz^{0,-2-}. One-electron transfer steps between the $n = (2-)$ and $(4+)$ states were studied by cyclic voltammetry and by EPR, UV-VIS-NIR spectroelectrochemistry for the structurally characterized *anti* isomer of $[\text{Cl}(\text{Q})\text{Ru}(\mu\text{-tppz})\text{Ru}(\text{Q})\text{Cl}](\text{PF}_6)_2$, **2**(PF_6)₂, the only configuration obtained. The combined investigations reveal that **2**²⁺ is best described as $[\text{Cl}(\text{Q}^\cdot)\text{Ru}^{\text{III}}(\mu\text{-tppz}^0)\text{Ru}^{\text{III}}(\text{Q}^\cdot)\text{Cl}]^{2+}$ with antiferromagnetic coupling between the ruthenium(III) and the iminosemiquinone components at each end. Metal-based spin as evident from large *g* factor anisotropy (EPR) and an intense inter-valence absorption band at 1850 nm in the near infrared (NIR) suggest that oxidation occurs at both iminosemiquinones to yield two Ru^{III} -bonded quinones, implying redox-induced electron transfer. Reduction takes place stepwise at the metal centers yielding iminosemiquinone complexes of $\text{Ru}^{\text{III,II}}$ as evident from radical complex EPR spectra with small ^{99,101}Ru hyperfine contributions. After complete metal reduction to ruthenium(II) the bridging ligand tppz is being reduced stepwise as apparent from typical NIR absorption bands around 1000 nm and from small *g* anisotropy of the monoanion $[\text{Cl}(\text{Q}^\cdot)\text{Ru}^{\text{II}}(\mu\text{-tppz}^\cdot)\text{Ru}^{\text{II}}(\text{Q}^\cdot)\text{Cl}]^-$.