

Role of intramolecular hydrogen bonding in the redox chemistry of hydroxybenzoate-bridged paddlewheel diruthenium (II,II) complexes

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Carboxylate bridged paddlewheel diruthenium complexes ($[\text{Ru}_2]$) have attracted attention for the use as functional modules such as redox-active component in metal-organic frameworks. For this purpose, tuning the electronic properties of $[\text{Ru}_2]$ unit has become key. Our groups have already demonstrated systematic tunability of the electronic properties in a series of F- or Cl-substituted benzoate-bridged $[\text{Ru}_2^{\text{II,II}}]$ complexes.^{1,2} Meanwhile, a phenolic OH group has electron-donating ability, in contrast to the electron-withdrawing abilities of F/Cl substituents. In particular, it often acts as a proton-donor for hydrogen bonding. Hence, the synthesis of an OH-substituted $[\text{Ru}_2^{\text{II,II}}]$ series was desirable, but has rarely been reported because of the difficulty of isolation in crystalline form.

In this study, a series of trans-heteroleptic $[\text{Ru}_2^{\text{II,II}}]$ complexes³ with various OH-substituted benzoate ligands, $[\text{Ru}_2((\text{OH})_x\text{PhCO}_2)_2(2,6-(\text{CF}_3)_2\text{PhCO}_2)_2(\text{THF})_2]$ were synthesized (Fig. 1a). The characterization of these compounds allowed a systematic analysis of the electronic property dependency on the OH substituent.⁴ In this heteroleptic series, the redox potential ($E_{1/2}$) of the $[\text{Ru}_2^{\text{II,II}}]/[\text{Ru}_2^{\text{II,III}}]^+$ couple in THF varies over a wide range, from -18 mV (vs. Ag/Ag^+) for *p*-OH to 432 mV for **2,6-(OH)₂**. The redox properties are linearly dependent on the acidity (pK_a) of the OH-substituted benzoic acids. The value of the Hammett constant σ_o for the *o*-OH substituent was determined to be 0.667 , indicating a strongly electron-withdrawing character, contrary to the expectation of electron-donating character for an OH group. The redox properties of the compounds were well explained in a framework of Hammett analyses (Fig. 1b) and were also consistent with their HOMO energy levels evaluated by DFT

calculations based on the atomic coordinates. The unexpected electron-withdrawing character of the *o*-OH groups could be attributed to the direct effect of intramolecular hydrogen bonding on the charge density on the carboxylate.

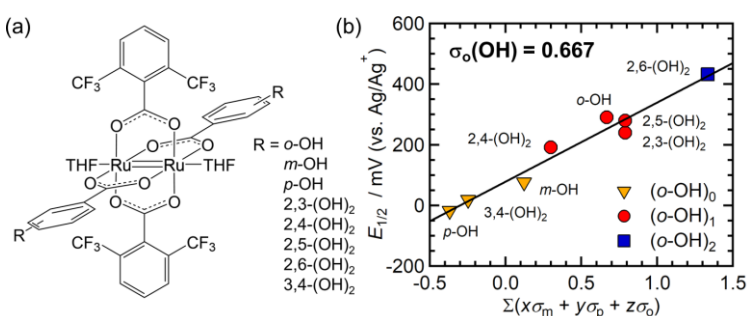


Fig. 1 (a) Scheme of molecular structure. (b) Plots of $E_{1/2}$ vs Hammett constant.

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