

Tuning of ruthenium(II) terpyridine complexes redox potential by coordination to heteroaryl-2-imidazole ligands

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Four new ruthenium(II) terpyridine complexes $[\text{RuCl}(\text{Himpy})(\text{tpy})]^+$ (**1**), $[\text{RuCl}(\text{Himpa})(\text{tpy})]^+$ (**2**), $[\text{RuCl}(\text{Himpm})(\text{tpy})]^+$ (**3**) and $[\text{RuCl}(\text{Himpz})(\text{tpy})]^+$ (**4**) have been synthesized and well characterized by UV-vis, ¹H-NMR, ESI-MS, and elemental analysis. Structures of (**1**) and (**4**) have been solved by X-ray crystallography. Electrochemical measurements were performed in order to know the influence of σ -donor/ π -acceptor properties of heteroaryl-2-imidazole ligands on redox potentials of all the complexes. Conductivity measurements performed in several solvents indicated 1:1 complex:counter-ion ratio. Electronic absorption spectra showed the MLCT energies to be bathochromically shifted compared to $[\text{Ru}(\text{tpy})_2]^{2+}$ ($\lambda = 475$ nm). Chemical shifts of all heteroaryl and imidazole protons were upfield and downfield shifted, respectively. Cyclic voltammetry displayed all the oxidation potentials around 0.3 V vs. Fc/Fc^+ couple, with complex (**1**) exhibiting the less positive oxidation potential.

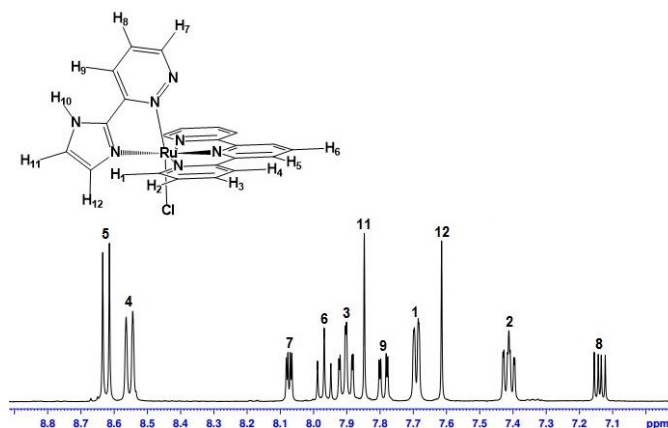


Figure 1. ¹H-NMR spectrum of (**2**) in DMSO-d₆.

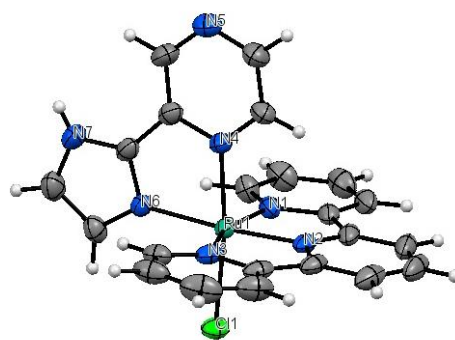


Figure 2. X-ray structure of (**4**).

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