

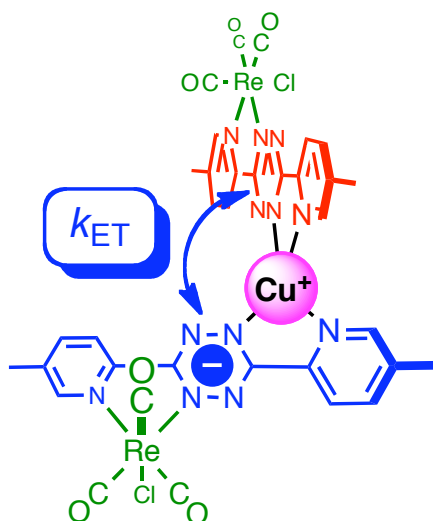
Ligand-Centered Mixed-Valency: Tetrazines Bridged by Cu(I)

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The first verified example of ligand mixed-valency is presented in which two redox-active tetrazine ligands are connected by a bridging Cu(I) ion. The ligand used, 3,6-bis-(5-methylpyridyl)-1,2,4,5-tetrazine, is monocoordinated to a $\{\text{Re}(\text{CO})_3\text{Cl}\}$ moiety, which serves as an IR-active group. A large separation (0.5 V) between consecutive reduction of the two ligands corresponds to a large comproportionality constant ($K_c \sim 10^8$) indicating the thermodynamic stability of the mixed-valent (MV) state, i.e., $(\text{L}^-)\text{-M}\text{-(L}^-)$. Chemical reduction of the complex provides the spectroscopic evidence ($\lambda_{\text{max}} = 2720 \text{ nm}$, $\epsilon = 1120 \text{ M}^{-1} \text{ cm}^{-1}$, $\text{FWHM} = 1260 \text{ cm}^{-1}$) for mixed-valency. Based on Marcus-Hush theory, the coupling constant was found to be small compared to its inorganic counterpart but the rate for electron transfer was found to be very large ($k_{\text{ET}} > 10^{11} \text{ s}^{-1}$). Variable temperature IR spectroscopy suggests that a Class III MV state is possible.