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論文名稱(中)	以比啉基二茂鐵與鈦氨的混價錯合物利用溶劑與取代基效應微調及反轉"金屬間電荷轉移"
論文名稱(英)	Tuning and "Inverting" Metal-to-metal Charge Transfer of Mixed-Valence Complexes Containing Ferrocenylpyridine and Rutheniumammine via Solvent Donicity and Substituent Effect
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關鍵字(中)	混價錯合物 溶劑給與效應 價間轉移 馬克斯-哈斯理論 漢米爾頓取代基效應
關鍵字(英)	mixed-valence complexes solvent donicity intervalence transfer Marcus-Hush Model Hammett substituent Effect
摘要(中)	<p>在此篇論文中，描述異核均相錯合物[R-Fc(4-Py)Ru(NH₃)₅](PF₆)₂ (R = H, Et, Br, acetyl; Fc(4-Py) = 4-ferrocenyl-pyridine)和[R₁-PyRu(NH₃)₄(4-Py)Fc-R₂](PF₆)₂ (R₁ = acetyl-, H-; R₂ = H-, ethyl)的合成方法及特性。使用氧化劑 ferrocenium hexafluorophosphate 將異核錯合物氧化成混價態，混價態行為屬於 class II，且[R-Fc(4-Py)Ru(NH₃)₅](PF₆)₂ 被氧化的是釕氨中心。介於 donor 和 acceptor 端將半波電位 ($\Delta E_{1/2}$)，$E_{1/2}(\text{Fe}^{\text{II/III}}) - E_{1/2}(\text{Ru}^{\text{II/III}})$ 近似於 ΔG_0 是非常好的假設，且半波電位非常明顯的與 Gutmann solvent donor number (DN)和 Hammett substituent constant (?)成線性關係。[R-Fc(4-Py)Ru(NH₃)₅]³⁺的價間轉移的溶劑與取代基效應，只與半波電位相關。</p>

光激發電子轉移的活化能 (EOP) 與半波電位 ($\Delta E_{1/2}$) 做圖的截距為核重組能 λ , $\lambda = 0.74 \pm 0.04$ eV 。光激發電子轉移的能量方程式 $E_{op} = \lambda + \rho G$, 在此自由能合併溶劑及取代基參數 , $\rho G = (\rho G)_{intrinsic} + (\rho G)_{solvent\ donicity} + (\rho G)_{substituent\ effect}$ 。其中 $(\rho G)_{intrinsic}$ 是 0.083 ± 0.045 eV , 是 $[H-Fc(4-Py)Ru(NH_3)_5]^{2+/3+/4+}$ 的半波電位與 DN 做圖的截距 , 而 $(\rho G)_{solvent\ donicity}$ 是 $[R-Fc(4-Py)Ru(NH_3)_5]^{2+/3+/4+}$ 的半波電位與 DN 作圖斜率的平均值 , $(\rho G)_{substituent\ effect}$ 為在同一溶劑之中 $\Delta E_{1/2}$ 與 λ 做圖的斜率平均值 。微調光激發電子轉移能量的經驗方程式 , $E_{op} = 0.82 + 0.019DN + 0.44 \sigma$ eV at 298 K , 實驗值及迴歸值得相對誤差為 6 % 。 $[R_1-py-Ru(NH_3)_4(4-py)Fc-R_2](PF_6)_2$ 的 $E_{1/2}(Ru^{II/III})$ 和 $E_{1/2}(Fc^{0/I})$ 的排序在 solvent donicity 的效應下會有反轉現象 。 $[R_1-pyRu(NH_3)_4(4-py)Fc-R_2](PF_6)_2$ 在 solvent donicity 的效應下 , 可以量測到 Fc^0-Ru^{III} 和 Fc^I-Ru^{II} 為起啟狀態的分子內光激發電子轉移的能量 。混價錯合物在 Frank-Condon barrier (Fc^0-Ru^{III} , Fc^I-Ru^{II}) 左端與右端是相類似 , 代表非常適合作為探討和說明 Marcus inverted region 的熱力學及光激發電子轉移的模型錯合物 。

摘要
(英)

A homogeneous series of heterobimetallic complexes of $[R-Fc(4-py)Ru(NH_3)_5](PF_6)_2$ ($R = H, Et, Br, Acetyl, Fc(4-py) = 4\text{-ferrocenyl-pyridine}$) and $[R_1-PyRu(NH_3)_4(4-Py)Fc-R_2](PF_6)_2$ ($R_1 = acetyl, H^-$; $R_2 = H^-, acetyl$) have been prepared and characterized. The mixed-valence species generated in situ using ferrocenium hexafluorophosphate as the oxidant show class II behavior, and the $[R-Fc(4-Py)Ru(NH_3)_5](PF_6)_2$ oxidized sites are ruthenium centered. $\lambda_{E_{1/2}}, E_{1/2}(Fe^{III}/Fe^{II}) - E_{1/2}(Ru^{III}/Ru^{II})$, an upper limit for ρG that is an energetic difference between the donor and acceptor sites, changes sharply and linearly with Gutmann solvent donor number(DN) and Hammett substituent constants(σ). The solvent-dependent and substituent-dependent IT bands were found to vary almost exclusively with $\lambda_{E_{1/2}}$. The activation energy of $[R-Fc(4-Py)Ru(NH_3)_5]^{3+}$ for optical electron transfer versus $\lambda_{E_{1/2}}$ plot yields a common nuclear reorganization energy (λ) of 0.74 ± 0.04 eV for this series. The equation that allows one to incorporate the effect of both solvent donicity and substituents on optical electron transfer is $E_{op} = \lambda + \rho G$ where $\rho G = (\rho G)_{intrinsic} + (\rho G)_{solvent\ donicity} + (\rho G)_{substituent\ effect}$. $(\rho G)_{intrinsic}$ with numerical value of 0.083 ± 0.045 eV was obtained from the intercept of $\lambda_{E_{1/2}}$ of $[H-Fc(4-py)Ru(NH_3)_5]^{2+,3+,4+}$ versus DN plot. $(\rho G)_{solvent\ donicity}$ was obtained from the average slopes of $\lambda_{E_{1/2}}$ of $[R-Fc(4-py)Ru(NH_3)_5]^{2+,3+,4+}$ versus DN plot and $(\rho G)_{substituent\ effect}$ was obtained from the average slopes of the corresponding $\lambda_{E_{1/2}}$ versus σ plot. The empirical equation allows one to finely tune E_{op} of this series was found to be $E_{op} = 0.82 + 0.019DN + 0.44 \sigma$ eV at 298 K and the discrepancy between the calculated and experimental data are less than 6%. Another closely related series of heterobimetallic complexes of $[R_1-pyRu(NH_3)_4(4-py)Fc-R_2](PF_6)_2$ ($R_1=H^-, Acetyl$; $R_2= C_2H_5^-, H^-$) were prepared in a similar fashion. They show interesting mixed-valence chemistry upon oxidation. The intramolecular electron transfer between $Fc^{0/I}$ and $Ru^{II/III}$ can invert the order via solvent donicity. These mixed-valence complexes, with the

	capability of reversible electron transfer and very similar back and forth Frank-Condon barriers (FcO-RuIII, FcI-RuII) shed more light on Marcus inverted region in addition to being good model compounds for probing thermal and optical electron transfer.
論文目次	封面 第一章緒論 一、分子內電子轉移的混價化學 二、分子內電子轉移的基礎理論 三、Gutmann Solvent-Donor Number 四、Hammett Constant of Inductive Effect 第二章實驗討論 主題 I Solvent-Dependent Studies of Intervalence Transfer of Mixed-Valence Complexes Containing Ferrocenylpyridine and Rutheniumammines 主題 II Tuning Metal-to-Metal Charge Transfer of Mixed-Valence Complexes Containing Ferrocenylpyridine and Rutheniumamine via Solvent Donicity and Substituent Effects 主題 III “Inverting” Metal-to-Metal Charge Transfer of Mixed-Valence Complexes Containing Ferrocenylpyridine and Rutheniumammines via Solvent Donicity and Substituent Effects 總結 第三章參考資料 儀器與藥品 合成 參考文獻 UV-vis Spectra CV NIR NMR
參考文獻	Tsun-Yang Liu, Yuan Jang Chen, Chih-Cheng Tai, and Ken Shin Kwan Inorg. Chem. 1999 38 674 Yuan Jang Chen, Ching-Hong Kao, She Jing Lin, Chih-Cheng Tai, and Ken Shin Kwan; Inorg. Chem. 2000,39 189 Yuan Jang Chen, Dung-Shien Pan, Chi-Fa Chiu, Jia-Xin Su, She Jing Lin and Keh Shin Kwan; Inorg. Chem. 2000,39 953 Chi-Fa Chiu, Chien-Liang Hwang, Dung-Shien Pan, Yuan Jang Cen and Ken Shin Kwan; J. Om. Chem. 1998 563 95
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