2-Hydroxypyridine 架橋水車型[$Ru_2^{II,III}$]二核錯体の酸化還元特性

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Redox properties of 2-hydroxypyridinate-bridged paddlewheel-type [$Ru_2^{II,III}$] complexes

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Paddlewheel-type diruthenium ([Ru_2]) complexes, especially, carboxylate-bridged [Ru_2] complexes, have widely been studied so far because of their specific redox property and intriguing magnetism. Meanwhile, a class of 2-hydroxypiridine (hp)-bridged [Ru_2] complexes has recently been attracted much attention (Fig. 1a). The hp-bridged [Ru_2] complexes have interesting characteristics such as their anisotropic structure, high redox activity, and wide-delocalized electron density over the pyridine ring. Hence, they have high potential to act as promising building units for the construction of functional frameworks. However, examples of hp-bridged [Ru_2] complexes are still limited. In this work, four hp-bridged [Ru_2] complexes [Ru_2(5-Rhp)$_4$Cl(Solv)] (**5-R; R = Br**, **Cl**, **NO_2**; Solv = coordinating solvent molecule) and [Ru_2(5-Br-4-Mehp)$_4$Cl(Solv)] (**5-Br-4-Me**) were newly synthesized and characterized (Fig. 1b). A reversible redox wave of [$Ru_2^{II,II}$]/[$Ru_2^{II,III}$]$^+$ was observed in CV for each complex in THF (Fig. 1c), which revealed a linear correlation between the redox potential ($E_{1/2}$ vs. Ag/Ag$^+$) and Hammett constant for the substituents introduced on the hp ligands (Fig. 1d). Systematic control of redox property was realized even in the class of hp-bridged [Ru_2] complexes.

Keywords : Paddlewheel-type Ru_2 Complex; Redox Properties; Substitution effect

水車型 Ru 二核錯体([Ru_2])は，特異的な酸化還元特性や興味深い磁気特性を示す分子ユニットであり，カルボン酸架橋錯体を中心に幅広く研究されてきた．一方，近年では 2-hydroxypyridine (hp)で架橋された[Ru_2]分子が注目を集めている(図 1a)[1]．hp 架橋[Ru_2]は，(1)異方的な分子構造，(2)酸化還元高活性，(3)ピリジン環上への電子非局在化，等の興味深い性質を示すことから，機能性配位骨格の構築素子としても大いに期待される．しかし，hp 架橋[Ru_2]錯体の報告例は意外と少ない．本研究では，5-位に置換基をもつ hp 架橋[$Ru_2^{II,III}$]$^+$化合物を合成し，酸化還元能の置換基効果について系統的検討を行った．[Ru_2(5-Rhp)$_4$Cl(Solv)] (**5-R; R = Br**, **Cl**, **NO_2**; Solv = 配位溶媒), [Ru_2(5-Br-4-Mehp)$_4$Cl(Solv)] (**5-Br-4-Me**)を合成，単離した．THF 中での CV では，[$Ru_2^{II,II}$]/[$Ru_2^{II,III}$]$^+$に対応する可逆な Redox 対が観測され(図 1c)，その半波電位($E_{1/2}$ vs. Ag/Ag$^+$) は Hammett 定数に対して良い相関を示した(図 1d)．hp 架橋[Ru_2]において酸化還元の系統的制御が可能であることが明らかになった．

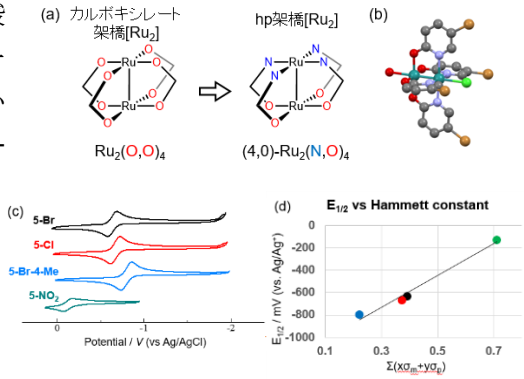

図 1 (a) [Ru_2]錯体模式図 (b) **5-Br** の結晶構造 (c) CV in THF (vs. Ag/Ag$^+$) (d) $E_{1/2}$ vs. Hammet 定数

1) A. Chakravarty *et al.*, *Inorg. Chem.*, **1985**, *24*, 1263.

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