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Preparation and Electrochemical Response of Poly(4-vinylpyridine)-Coordinated Oxo-acetato Triruthenium Cluster Film

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The trinuclear ruthenium cluster $[Ru^{III}_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6\text{-}(pyridine)_2(CH_3OH)]^+$ was incorporated into poly(4-vinylpyridine) through substitution of the pyridyl residue for CH_3OH to form a new macromolecular complex, which showed distinctive reversible cyclic voltammographic waves at -0.05 and +0.95 V vs. SCE in aqueous CF_3COO^- medium at pH 3, when coated on a glassy carbon electrode as a transparent film.

Ruthenium analogs of the widely known trinuclear oxo-acetato metal complexes,1) $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6L_3]^+$ (L = H_2O, pyridine, etc.) are of great interest, particularly in multiple one-electron redox behaviour due to metal $d\pi\text{-}O(\mu_3)p\pi$ interactions.2-6) These also catalyse some organic oxidations in solution7) and reductions in the polymer-supported system,8) in which the trinuclear unit was claimed to be introduced to resin through carboxylate but structurally rather poorly characterized. On the other hand, electrochemical studies of polymer-metal complexes attached to electrode surfaces are prominent but the complexes are substantially limited to mononuclear ones with a single redox step.9)

We tried to introduce the trinuclear unit into poly(4-vinylpyridine) at the terminal ligand (L) position in a search for new macromolecular derivatives of the celebrated cluster complex and also for electrochemical responses bearing potential applications of the complex as a redox mediator to photoelectrocatalytic redox polymer film systems,10) since the multiple redox potentials are "tunable" by the choice of the terminal ligands.6)

Ten mg of $[Ru^{III}_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_2(CH_3OH)](PF_6)$ (**1**, py = pyridine)4a) in CH_2Cl_2 (4 ml) and 42 mg of poly(4-vinylpyridine-co-styrene) (Aldrich, styrene content 10%, PVP) in $CHCl_3$ (6 ml) were mixed at the ratio [complex] : [py-residue] = 1 : 36, stirred for 24 h at room temperature and evaporated to dryness. The residue was washed with CH_3CN to remove unreacted complex (**1**), which is very soluble in CH_3CN,

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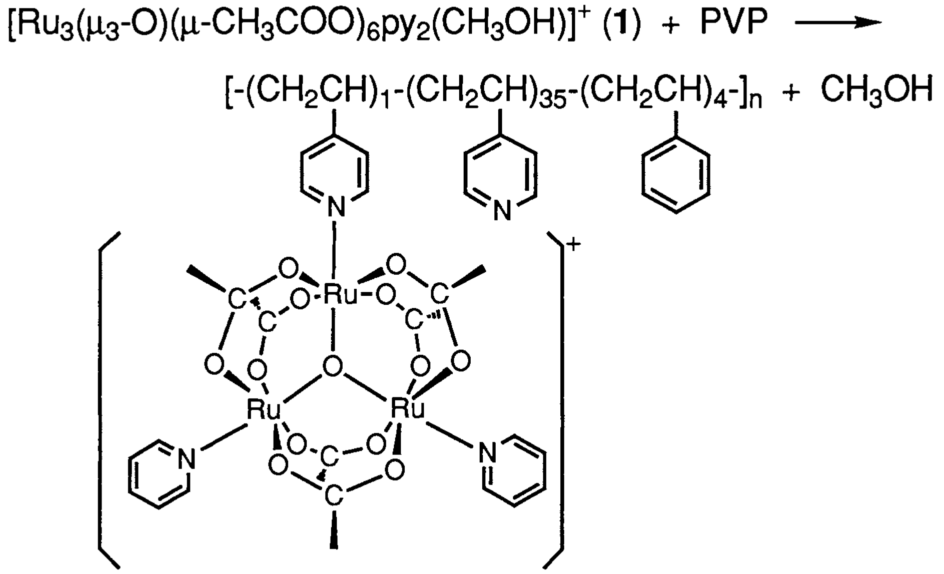
but the washings showed only very weak blue color. During the course of the reaction, the absorption maximum of the reaction mixture was shifted from 679 nm (ε 4400 M^{-1} cm^{-1}) to 690 (5620) in the mixed solvent (M = mol dm^{-3}). These values are in accordance with 685 (4420) for **1** and 692 (5800) for $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$ in CH_2Cl_2.[4a)] The macromolecular complex was soluble in $CHCl_3$. From these observations, we conclude that reaction (1) proceeds smoothly and quantitatively.



$$[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6py_2(CH_3OH)]^+ \ (\mathbf{1}) + PVP \longrightarrow [\text{-}(CH_2CH)_1\text{-}(CH_2CH)_{35}\text{-}(CH_2CH)_4\text{-}]_n + CH_3OH \quad (1)$$

Similar results were obtained for the known trinuclear derivatives,[4a,b)] $[RU(CO)(CH_3OH)_2]$ (**2**), $[RU(CH_3OH)_3](CH_3COO)$ (**3**), $[RU(CO)(py)_2]$ (**4**), $[RU(py)_3]$ (**5**) and $[RU(py)_3](PF_6)$ (**6**), where RU denotes $Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6$ moiety in which the formal oxidation states of Ru_3 are (III,III,III) for **3** and **6**, and (II,III,III) for **2**, **4**, and **5**. The reaction mixture was refluxed for a few hours to assure pyridyl substitution for the pyridine ligands (**4**, **5**, and **6**), while stirred at room temperature for the CH_3OH ones (**2** and **3**), on the basis of our recent kinetic data on py/py exchange and py/CH_3OH substitution of these complexes by NMR.[11)] Appreciable colour change of the mixture did not take place for the py complexes, while distinctive change did for the CH_3OH ones. However, the resulting compounds were insoluble in ordinary solvents, once the mixture was evaporated to dryness. Since these complexes have two or three substitutable sites by the pyridyl residue, the cross-linking between the polymer chains can take place and bring about the insolubility.[12)]

The macromolecular complex from **1**(52 mg) was dissolved in $CHCl_3$ (1 ml), filtered through a membrane filter, and cast onto a glassy carbon plate or a Nesa-glass (40 x 40 mm) to form an optically transparent film.[10)] Its thickness and surface coverage of the cluster was ca. 1 μm and 2 x 10^{-8} mol cm^{-2}, respectively, as determined by spectroscopy at the maximum (690 nm). The coated glassy carbon electrode gave the cyclic voltammogram (Fig. 1) at a scan rate 20 mV s^{-1} with an SCE

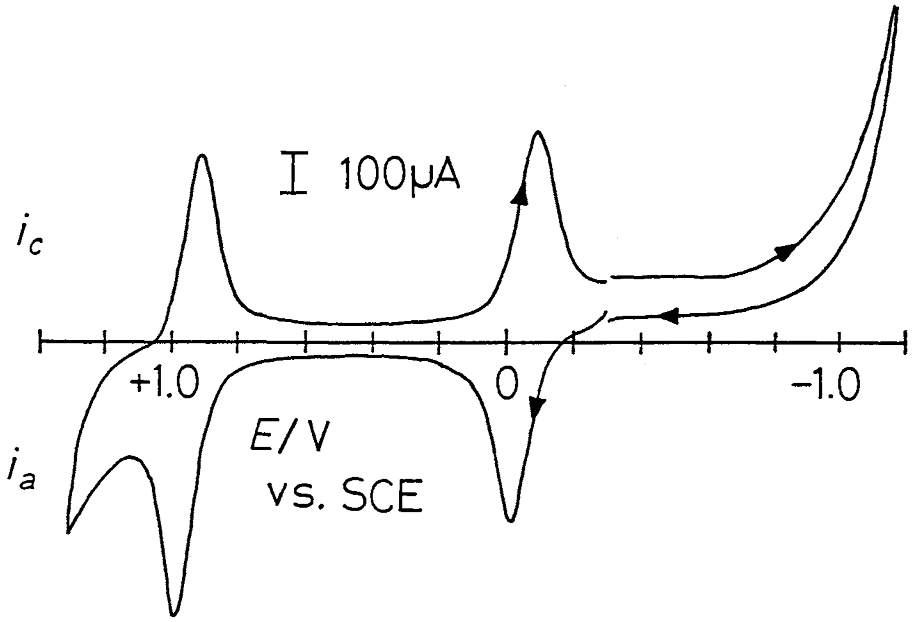


Fig. 1. Cyclic voltammetric response of $[Ru^{III}_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(pyridine)_2(CH_3OH)]^+$-incorporated poly(4-vinylpyridine) film on a glassy carbon electrode, in aqueous $Na(CF_3COO)$ medium(0.1 M, pH 3) with an SCE and a Pt wire. Scan rate : 20 mV s^{-1}.

and a Pt-wire in aqueous $Na(CF_3COO)$ (0.1 M) medium at pH 3. The curve remained unchanged through the repeated scans for an hour. Two essentially reversible waves at -0.05 and +0.95 V vs. SCE (ΔE = ca. 80 mV for both) can be compared with those of **5** (and **6**) at -0.05 and +0.97 V vs. SSCE in CH_3CN[4a] and assigned to the processes of Ru_3(III,III,III)/(II,III,III) and Ru_3(III,III,IV)/(III,III,III), respectively. This is the first observation that cluster complex incorporated into polymer shows clear reversible and multiple redox processes. When Cl^-, ClO_4^-,or PF_6^- was used in place of CF_3COO^-, the current was remarkably decreased and the reversibility heavily damaged. It is known that redox polymer prepared from $[Fe(CN)_5(OH_2)]^{3-}$ and poly(4-vinylpyridine) gives effective electrochemical response with $Na(CF_3COO)$ as supporting electrolyte.[9a] The mobility of anions in the polymer film might be an important factor for the present response.

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