

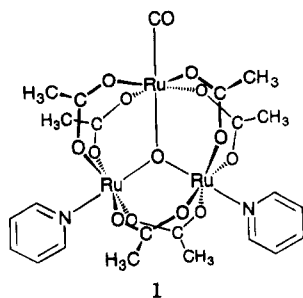
In-Situ FT-IR Spectroelectrochemical Study of the Trinuclear Complex $[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{CO})(\text{pyridine})_2]$ in Acetonitrile

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One of the most important aspects of metal cluster complexes is their multistep multielectron redox behavior. Assignment of the redox sites during redox processes is basically important in understanding their electronic state and catalytic activity. Vibrational spectroscopy that is useful for this purpose has been applied for some chemically stable oxidation states of various metal cluster complexes.¹ In-situ FT-IRRAS (Fourier transform infrared reflection absorption spectroscopy) is now drawing great attention in electrochemistry.^{1,2} It can provide important information about redox states, chemical bonding, and mass transport of reactant and product species in the thin layer between electrode and window. Its application to redox systems involving chemically unstable oxidation states is also important.¹ In this paper, we wish to report successful application of in-situ FT-IRRAS measurements with a thin-layer cell to a series of four different oxidation states of a monocarbonyl trinuclear ruthenium complex, $[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{CO})(\text{py})_2]$ (py = pyridine) (**1**).^{3,4} The higher oxidation states of **1** are unstable and are difficult to characterize by other techniques.



Complex **1** is a member of oxo-centered carboxylato-bridged trinuclear ruthenium complexes which are among the most promising simple systems that display reversible multistep redox behavior^{3–7} and act as catalysts for certain organic reactions.⁸

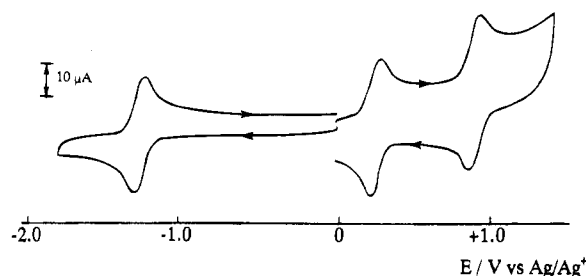


Figure 1. Cyclic voltammogram of $[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{CO})(\text{py})_2]$ (ca. 0.5 mM) in 0.1 M (TBA)PF₆–acetonitrile solution. Glassy-carbon working, Pt auxiliary, and Ag/Ag⁺ ((AgClO₄) = 0.1 M) reference electrodes were used. The scanning rate was 100 mV/s.

Complex **1** was isolated only as a neutral Ru^{II}Ru^{III}₂ state, which shows electrochemically reversible consecutive one-electron processes with net charges from –1 to +2 in acetonitrile.

The cyclic voltammogram of **1** measured in 0.1 M tetrabutylammonium hexafluorophosphate ((TBA)PF₆) shown in Figure 1 is in good agreement with an earlier result.⁴ The delocalized $d\pi(\text{Ru})-p\pi(\mu_3\text{-O})$ molecular orbital description was applied for triruthenium complexes such as $[\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}_2(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{py})_3]$.⁴ It was pointed out, however, that the CO complex exhibits spectroscopic and redox characteristics notably different from those of other triruthenium(II,2III) complexes⁴ and was considered to have localized Ru(II)–CO state. This is probably due to the strong back-donating nature of the CO ligand.^{4,9,10} It would be interesting to know how such a localized electronic state is affected during successive redox processes. Attempts to isolate species with oxidation states other than Ru^{II}Ru^{III}₂ were not successful due to their chemical instability, although the redox processes are electrochemically reversible as shown in Figure 1. In-situ spectroelectrochemical measurements of UV–visible absorption spectra of the oxidized species using the thin-layered cell also suffered from partial dissociation of the CO ligand from the trinuclear core during electrolysis. Bulk electrolysis in acetonitrile at ca. 600 mV gave a spectrum which is essentially identical to that of $[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{CH}_3\text{-CN})(\text{py})_2]^+$. By using the FT-IRRAS technique, however, we were able to observe $\nu(\text{CO})$ values of the oxidized species even though the decomposition proceeded partially.

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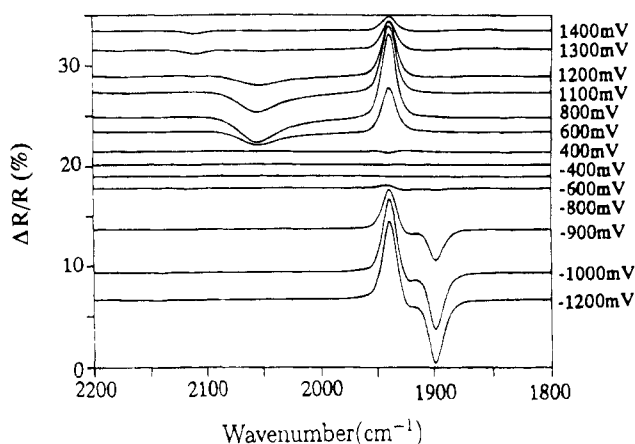


Figure 2. In-situ FTIR spectra of $[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{CO})(\text{py})_2]$ (ca. 0.5 mM) in 0.1 M (TBA)PF₆-acetonitrile solution. The spectra were obtained as difference spectra between the reference potential (0 mV vs SSCE) and various potentials shown above. See text for details.

The in-situ FT-IRRAS measurements were carried out on a Bio-Rad FTS-30 equipped with a liquid-N₂-cooled HgCdTe detector. A thin-layer IR spectroelectrochemical cell¹¹ with a CaF₂ window was used for in-situ IR and electrochemical measurements. The incidence angle of the infrared beam was approximately 65°. A mirror-finish gold disk used as the working electrode was pushed against the CaF₂ windows. The liquid layer between the electrode and the windows was very thin, only about 1 μm, so that redox processes of solution species were expected to be completed rapidly when the electrode potential was changed. The potentials are referred to the sodium saturated calomel electrode (SSCE). A total of 512 interferograms with 4 cm⁻¹ resolution were collected at each potential.

Figure 2 shows the differential IR spectra of **1** in acetonitrile at various applied potentials. The reference spectrum was the one at 0 V, where the Ru-CO complex exists as (II,2III). A reference spectrum was taken each time a measurement was made at a certain potential, so that the contribution from the decomposition product was minimized. Due to partial decomposition, particularly in the more positive potential region (corresponding specifically to the +1 and +2 states), quantitative comparison of the difference spectra at various potentials is not possible. However, we successfully assigned the $\nu(\text{CO})$ values at different oxidation states by using the measurements. All the peaks assigned to $\nu(\text{CO})$ disappeared as the original (II,2III) complex regenerated on changing the potential back to

0 V. It is noteworthy that all four types of $\nu(\text{CO})$ values corresponding to the respective redox states were clearly observed in the cyclic voltammogram. The $\nu(\text{CO})$ values for the species with net charges of -1, 0, +1, and +2 were 1900, 1940, 2055, and 2110 cm⁻¹, respectively.^{12,13} In the region of +1 and +2 states, an additional peak assignable to CO₂ was observed at 2340 cm⁻¹ as decomposition proceeded. Although liberation of CO at higher oxidation states is expected, the peak assignable to free CO was not detected due to possible insensitivity of free CO to the measurements. It is concluded that there is a minor pathway involving CO₂ formation in addition to the decomposition accompanied by CO liberation. Contaminated water may play a role here.

Although we cannot correlate the absolute value of $\nu(\text{CO})$ with the oxidation state of the ruthenium ion which is coordinated by CO, the difference in the values between the neighboring oxidation states is informative. A significant difference between the $\nu(\text{CO})$ values of the neutral and +1 species indicates that substantial change in electron density takes place on the ruthenium ion with CO during the 0/+1 process. Namely, the electronic state of the trinuclear complex in the +1 state may be expressed by (3III) rather than the localized (II,III,IV) (Ru^{II}(CO)-Ru^{III}Ru^{IV}(py)) description. This should cause a considerable weakening of a back-donation of an electron to the CO ligand. Further oxidation would give the delocalized (2III,IV) state so that much less change in the electron density of the ruthenium ion with CO would be expected. The 0/-1 process would involve the reduction of the Ru^{III}₂(py) site to give Ru^{II}Ru^{III}(py),¹⁴ while the Ru^{II}(CO) site is less affected.

The present work clearly demonstrates the usefulness of in-situ FT-IR spectroelectrochemical techniques in evaluating the redox sites of multielectron redox systems involving less stable redox states. In-situ FT-IRRAS measurements certainly provide specific information such as $\nu(\text{CO})$ values in this case from mixtures where decomposition may proceed.

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 (14) It is not possible to distinguish between the localized Ru(II)-Ru(III) and the delocalized Ru^{II}Ru^{III} state of the pyridine-coordinated sites in the present work. Further studies using other vibrational modes or other spectroscopic techniques to distinguish between the two alternatives would be desirable.