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In-Situ SNIFTIR Spectroelectrochemical Study of Metal Cyano-Complexes in the Presence of Trications

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From SNIFTIR spectroscopic and electrochemical measurements, ion-paired species of $Fe(CN)_6^{3-/4-}$ and $Ru(CN)_6^{3-/4-}$ with H^+ and Al^{3+}, and of $W(CN)_8^{3-/4-}$ and $Mo(CN)_8^{3-/4-}$ with Ga^{3+} and In^{3+} were clearly detected for the first time (except for the protonation reaction of $Fe(CN)_6^{4-}$), and some of their properties in solution are discussed.

Some cyano-complexes of such metals as Fe, Ru, W and Mo, have been widely used as typical reversible redox couples.[1-3] However, redox behavior of such complexes has not yet been elucidated well. For example, for the $Fe(CN)_6^{3-/4-}$ couple, both electrochemical behavior and interfacial infrared (IR) spectra have recently been reported[1,4,5] to be somewhat complicated depending on cations added[1] and on intermediates adsorbed on the electrode surface during the charge transfer.[5] Cations would change the structure of the redox species in solution as well as the interfacial structure of the electrode surface. Since the C-N stretching vibration, ν(C-N), gives a strong IR absorption, in-situ IR spectroscopic measurements would be one of powerful techniques to understand electrochemical behavior of metal cyano-complexes at the molecular level. However, no IR spectroscopic study has yet been reported so far on metal cyano-complexes other than the $Fe(CN)_6^{3-/4-}$ system. In the present paper, the first observations are reported on the so-called subtractively normalized interfacial Fourier transform infrared (SNIFTIR)[6] spectroelectrochemical behavior of several metal cyano-complexes in the presence of H^+ or trications such as Al^{3+}, Ga^{3+} and In^{3+}.

$K_4[Fe(CN)_6]$ and $K_4[Ru(CN)_6]$ were obtained from Alfa Products. $K_4[W(CN)_8]$ and $K_4[Mo(CN)_8]$ were prepared according to the literatures.[7] Further recrystallization of these compounds from water was carried out, when necessary, to be >99.9% in purity.

Cyclic voltammetry was carried out in a 0.1 M NaCl solution at a pyrolytic graphite (PG) or a Pt electrode. The counter and the reference electrodes used were a Pt plate and an SCE, respectively. SNIFTIR spectra were obtained using a JASCO FTIR-3 spectrophotometer with a reflectance attachment (PR-41S) and a liquid nitrogen cooled Hg-Cd-Te (MCT) detector. The spectrometer was connected to an NEC PC-9801RX4 computer system. The data from 100 times scans of the interferometer were accumulated (ca. 4 min) at a given potential (E_i) and a base reference potential (E_0), alternately, for five times. Each set of data was then averaged. The averaged datum (R_i) at E_i was normalized to $\Delta R/R$ ($=(R_i-R_0)/R_0$) by dividing by that (R_0) at E_0. The upward (downward) signals of $\Delta R/R$ mean the decrease (increase) in absorbance at E_i than at E_0 (= 0 V vs. SCE). A thin layer type spectroelectrochemical cell with a CaF_2 prism window having 10 mm thick and 60° beveled edges was used. The working electrode was a polycrystalline Pt disk of ca. 8 mm diameter, of which surface had been mirror polished with 0.05 µm alumina powder followed by ultrasonic cleaning before each measurement. The spectra reported in the present paper were obtained using p-polarized light, but note that the obtained signals came from the thin layer solution in front of the electrode and were not due to adsorbed species on the electrode.

Cyclic voltammograms of $Fe(CN)_6^{3-/4-}$, $Ru(CN)_6^{3-/4-}$, $W(CN)_8^{3-/4-}$, and $Mo(CN)_8^{3-/4-}$ couples showed usual behavior for a reversible one-electron transfer reaction with the formal redox potentials ($E^{0'}$) of 0.18, 0.70, 0.27, and 0.53 V (vs. SCE), respectively, in a 0.1 M NaCl solution. However, in acid solutions of pH below 3, $E^{0'}$ values of both $Fe(CN)_6^{3-/4-}$ and $Ru(CN)_6^{3-/4-}$ couples shifted toward positive potentials (by ca. 160 mV for $Fe(CN)_6^{3-/4-}$ and 110 mV for $Ru(CN)_6^{3-/4-}$ at pH 1, see Fig. 1). Also, for these complexes, the heterogeneous electron transfer rate constant (k_{sh}) estimated from the peak separation of the cyclic voltammograms at pH 1 was about twice larger than that at pH >3. In the SNIFTIR spectra of both $Fe(CN)_6^{4-}$ and $Ru(CN)_6^{4-}$, the ν(C-N) frequency shifted toward larger wavenumbers in acid solutions, as was reported[1)] for $Fe(CN)_6^{4-}$, indicating protonation to cyanide ions took place. Interestingly, on the other hand, for $W(CN)_8^{3-/4-}$ and $Mo(CN)_8^{3-/4-}$, no influence of pH (down to pH 1) on $E^{0'}$, K_{sh} and the ν(C-N) frequency in SNIFTIR spectra was observed, meaning an

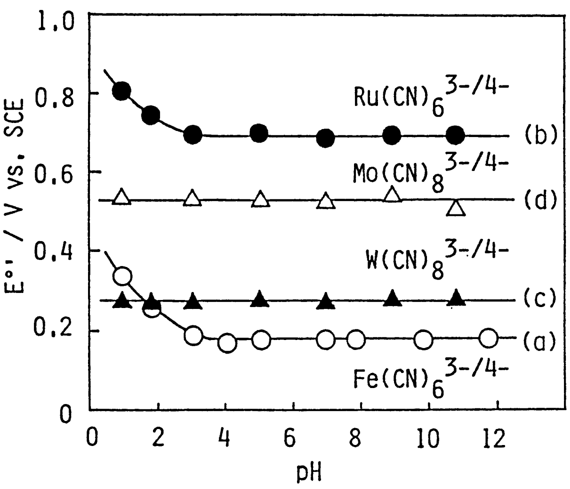

Fig. 1. pH dependence of $E^{0'}$ of cyano-complexes at 25 °C. The Britton-Robinson buffer solutions with 0.1 M NaCl and a 0.1 M HCl solution (for pH 1) were used.

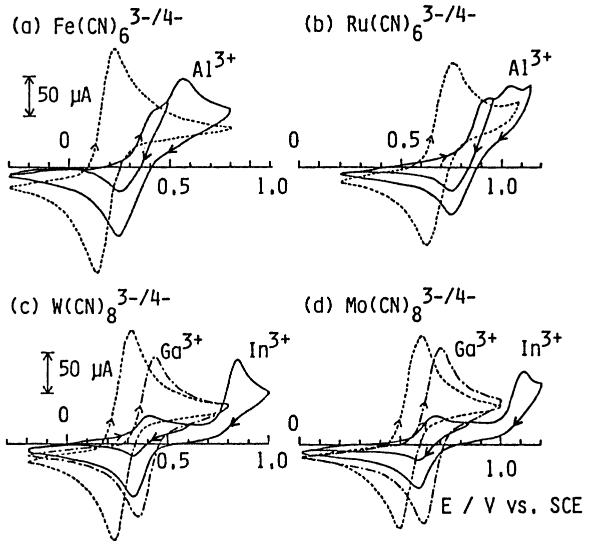

Fig. 2. Cyclic voltammograms of 5 mM cyano-complexes at a PG electrode at 50 mV/s in a 0.1 M NaCl solution in the absence (---) and presence of the indicated trications (0.1 M).

interaction between proton and cyanide ions of these complexes is negligible.

In the presence of 0.1 M Al^{3+}, $Fe(CN)_6^{4-}$ and $Ru(CN)_6^{4-}$ showed two ill-defined but appreciable anodic peaks on cyclic voltammograms at more positive potentials (Fig. 2, a and b). Also, in SNIFTIR spectra, two ν(C-N) upward peaks developed at higher wavenumbers with increasing the Al^{3+} concentration (Fig. 3). These results suggest the presence of at least two distinguishable species, which would be attributable to mono- and di- (or multi-) Al^{3+} ion-paired species of $Fe(CN)_6^{4-}$ and of $Ru(CN)_6^{4-}$. The shifts in $E^{0'}$ and ν(C-N) observed seem to be reasonable for the subsequent formation of mono- and di- (or multi-) ion-paired species, where the ion-pair formation would occur at all CN^- ions in dynamically equivalent. On the other hand, no SNIFTIR spectral change for the $W(CN)_8^{3-/4-}$ and $Mo(CN)_8^{3-/4-}$ couples was seen in the presence of 0.1 M Al^{3+}, although the $E^{0'}$ values slightly shifted toward positive direction (ca. 40 mV) and k_{sh} increased by ca. 3 times. These results show that an interaction between Al^{3+} and these octacyano-complexes is rather weak, but the interfacial redox behavior changes.

Both Ga^{3+} and In^{3+} interacted strongly with $Fe(CN)_6^{4-}$ and $Ru(CN)_6^{4-}$ to give white precipitates, while for $W(CN)_8^{4-}$ and $Mo(CN)_8^{4-}$ no precipitation occurred. In SNIFTIR spectra, two or three new upward peaks at higher wavenumbers appeared depending on the concentration of Ga^{3+} or In^{3+} added (Fig. 4). This suggests again the subsequent formation of ion-paired species of $W(CN)_8^{4-}$ and $Mo(CN)_8^{4-}$ with these trications. In the presence of In^{3+} cyclic voltammograms of these complexes showed an oxidation wave at highly positive potentials. The second anodic wave has no reversible re-reduction wave, but gave an increase in reduction current at the potential for the first wave (Fig. 2, c and d). This indicates the second In^{3+} bound to the complexes was released during oxidation of the di- ion-paired species in the time scale of the voltammetric measurement. The species,

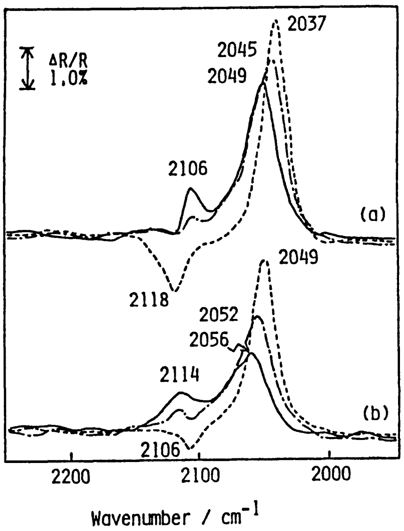

Fig. 3. SNIFTIR spectra of 5 mM (a) $Fe(CN)_6^{4-}$ (E_i=0.5 V) and (b) $Ru(CN)_6^{4-}$ (E_i=0.85 V) in a 0.1 M NaCl solution in the absence (---) and presence of 0.1 M (——) or 0.02 M(-・-) Al^{3+}.

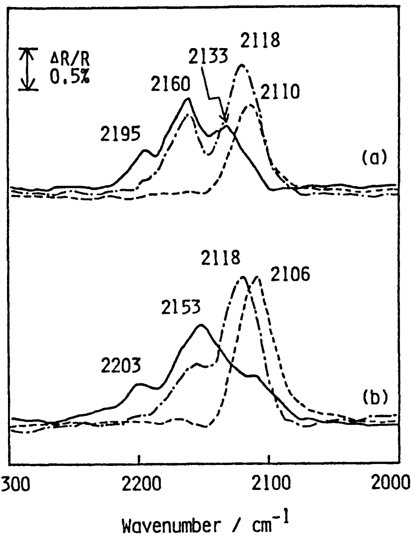

Fig. 4. SNIFTIR spectra of 5 mM (a) $Mo(CN)_8^{4-}$ (E_i=0.7 V) and (b) $W(CN)_8^{4-}$ (E_i=0.5 V) in a 0.1 M NaCl solution in the absence (---) and presence of 0.1 M Ga^{3+} (-・-) or In^{3+} (——).

which was distinguishable in the SNIFTIR spectra with a peak around 2200 cm^{-1} in the presence of 0.1 M In^{3+}, would have three ion-pairing In^{3+} ions. This species probably gives oxidation potential too positive to be detected on a cyclic voltammogram under the present experimental conditions. In the presence of Ga^{3+}, however, no separated redox wave on cyclic voltammograms of the octacyano-complexes was observed, although the redox potential shifted to be more positive (see Fig. 2, c and d). This can be explained in terms of an equilibrium between mono- and di- ion-paired species with rapid exchange.

Addition of 0.1 M Al^{3+}, Ga^{3+}, or In^{3+} caused also the pH change of the solution to more acidic to be ca. 3 to 3.5. However, since no significant change in electrochemical or spectroelectrochemical behavior of the cyano-complexes used took place by such a change in pH of the solutions (see Fig. 1), the observed effects of trications do not include the pH effect.

In conclusion, SNIFTIR spectroscopic and electrochemical measurements showed that cations interact more strongly with $Fe(CN)_6^{3-/4-}$ and $Ru(CN)_6^{3-/4-}$ complexes than with $Mo(CN)_8^{3-/4-}$ and $W(CN)_8^{3-/4-}$ ones. H^+ and Al^{3+} form ion-paired species with the former complexes, but have no strong interaction with the latter. On the other hand, on addition of Ga^{3+} and In^{3+} the former complexes precipitated, but the latter complexes generated a few soluble ion-paired species. To evaluate the electrochemical behavior of metal cyano-complexes in the presence of cations, two possibilities that the changes in the bulk species and in the interfacial structure of the electrode surface should be taken into account. In-situ IR spectroscopic technique provides useful information about the properties of ion-paired species in solution and about the interfacial redox behavior.

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