Resonance Raman Spectra of Iron(II) Complexes with 4,4'-Didodecyloxy-2,2'-bipyridine and 4,4'-Dioctadecyloxy-2,2'-bipyridine

Andrzej T. Kowal\textsuperscript{a,*} and Jacek Skarżewski\textsuperscript{b}

\textsuperscript{a} Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University, PL-50-370 Wrocław, Poland

\textsuperscript{b} Institute of Organic and Physical Chemistry, Technical University, PL-50-370 Wrocław, Poland

(Received 14 December 1983. Accepted 29 February 1984)

The resonance Raman spectra of Fe(LC\textsubscript{12})\textsubscript{3}Cl\textsubscript{2} and Fe(LC\textsubscript{18})\textsubscript{3}Cl\textsubscript{2} (where LC\textsubscript{12} and LC\textsubscript{18} denote 4,4'-didodecyloxy-2,2'-bipyridine and 4,4'-dioctadecyloxy-2,2'-bipyridine, respectively) have been measured along with their excitation profiles. The exciting lines of an Ar\textsuperscript{+} laser have been used. The bands appearing in the RR spectra within 1 200--1 600 cm\textsuperscript{-1} (expected to arise from the bipy moiety C--N and C--C vibrations) suffer the greatest resonance enhancements. Both depolarization ratios of the Raman bands and excitation profiles reveal the interaction of the resonant electronic states.

[Keywords: 4,4'-Didodecyloxy-2,2'-bipyridine; 4,4'-Dioctadecyloxy-2,2'-bipyridine; Excitation profiles; Iron (II); Resonance Raman spectra]

Resonanz-Raman-Spektren von Eisen(II)-Komplexen mit 4,4'-Didodecyloxy-2,2'-bipyridin und 4,4'-Dioctadecyloxy-2,2'-bipyridin

Es wurden die Resonanz-Raman-Spektren von Fe(LC\textsubscript{12})\textsubscript{3}Cl\textsubscript{2} und Fe(LC\textsubscript{18})\textsubscript{3}Cl\textsubscript{2} zusammen mit ihren Excitationsprofilen gemessen (LC\textsubscript{12} und LC\textsubscript{18} bedeuten 4,4'-Didodecyloxy-2,2'-bipyridin bzw. 4,4'-Dioctadecyloxy-2,2'-bipyridin). Dazu wurde ein Ar\textsuperscript{+}-Laser benutzt. Die Banden im Bereich von 1 200--1 600 cm\textsuperscript{-1}, die den C--N- und C--C-Vibrationen zuzuordnen sind, zeigen die größten Resonanzverstärkungseffekte. Sowohl die Depolarisationsverhältnisse als auch die Excitationsprofile dokumentieren die Wechselwirkung in den resonierenden elektronischen Zuständen.

Introduction

Resonance Raman spectra of bis- and tris-\(\alpha\)-diimine complexes of Fe(II) and Os(II) were studied extensively\textsuperscript{1--3} in order to resolve the ambiguities in the assignment of their absorption bands\textsuperscript{4--7}. Inspection
of both excitation profiles of the complexes being studied and the depolarization ratios of the Raman bands has revealed that the shoulders on the high-frequency side of the main electronic band ($^{1}E \rightarrow ^{1}A_{1}$) of these compounds are almost exclusively due to vibronic transitions.

Recently, several ruthenium(II) complexes with surfactant bipy derivatives such as dioctadecyl or bis(dihydrocholesteryl) esters of $4,4'$-dicarboxy-2,2'-bipyridine were believed to be useful as catalysts of water photolysis for solar energy conversion systems. These complexes, however, were shown to decompose gradually during the photolysis process because of hydrolysis of the ester groups. The aim of the present study was to apply resonance Raman spectroscopy to the iron(II) complexes of long aliphatic chain bipy derivatives, Fe($LC_{12}$)$_{3}$Cl$_{2}$ and Fe($LC_{18}$)$_{3}$Cl$_{2}$ in the hope of monitoring the influence of a long-chained ligand on the enhancement of Raman bands originating from bipy moiety vibrations. Moreover, it seems interesting to determine whether or not the enhanced modes derive their intensity from the electronic state involved in the transition observed at ca. 19 500 cm$^{-1}$.

**Experimental**

**Syntheses**

Both ligands, $4,4'$-didodecyloxy-2,2'-bipyridine and $4,4'$-dioctadecyloxy-2,2'-bipyridine were synthesized according to a described procedure.

Iron(II) complexes, Fe($LC_{12}$)$_{3}$Cl$_{2}$ and Fe($LC_{18}$)$_{3}$Cl$_{2}$ were prepared by the following method:

Anhydrous FeCl$_{2}$ (0.005 mol) and $LC_{12}$ ($LC_{18}$) (0.001 mol) were placed in a round-bottomed flask containing 100 cm$^{3}$ of CHCl$_{3}$. The mixture was refluxed for 0.5 h. The resulting deep-red solution was filtered off and concentrated to ca. 25 cm$^{3}$ in a rotary evaporator connected to a water aspirator. Then the solution was diluted with absolute ethanol (1:1) and concentrated further until its volume was reduced to ca. 20 cm$^{3}$. After cooling at 0 °C for 24 h wine-red crystals formed. The product was collected, washed three times with 3 cm$^{3}$ portions of ice-cold ethanol and dried over P$_{2}$O$_{5}$. The purity of the complexes was checked by elemental analyses.

Calculated for Fe($C_{34}H_{66}O_{2}N_{2}$)$_{3}$Cl$_{2}$: Fe 3.28, C 72.0, H 9.96, N 4.94. Found: Fe 3.61, C 71.8, H 9.00, N 5.28.

Calculated for Fe($C_{46}H_{80}O_{2}N_{2}$)$_{3}$Cl$_{2}$: Fe 2.97, C 74.4, H 10.57, N 4.27. Found: Fe 2.53, C 75.1, H 10.97, N 3.81.

**Spectral Measurements**

Resonance Raman spectra were measured on a Jeol JRS-S1 spectrometer equipped with a Coherent Radiation CR-3 argon ion laser using exciting lines between 476.5 nm and 514.5 nm. A typical exciting line power measured at the sample was ca. 100 mW. The spectra were measured in $1.5 \cdot 10^{-3} M$ CHCl$_{3}$ solutions employing the spinning cell technique (ca. 1600 rpm). The 1 221 cm$^{-1}$ band of chloroform was taken as an internal standard. The intensities