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

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The resonance *Raman* spectra of $Fe(LC_{12})_3Cl_2$ and $Fe(LC_{18})_3Cl_2$ (where LC_{12} and LC_{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^+ laser have been used. The bands appearing in the *RR* spectra within 1 200–1 600 cm^{-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 $Fe(LC_{12})_3Cl_2$ und $Fe(LC_{18})_3Cl_2$ zusammen mit ihren Excitationsprofilen gemessen (LC_{12} und LC_{18} bedeutet 4,4'-Didodecyloxy-2,2'-bipyridin bzw. 4,4'-Dioctadecyloxy-2,2'-bipyridin). Dazu wurde ein Ar^+-Laser benutzt. Die Banden im Bereich von 1 200—1 600 cm^{-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-α-diimine complexes of Fe(II) and Os(II) were studied extensively[1—3] in order to resolve the ambiguities in the assignment of their absorption bands[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 ($^1E \leftarrow {}^1A_1$) of these compounds are almost exclusively due to vibronic transitions[1].

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[8,9]. These complexes, however, were shown to decompose gradually during the photolysis process because of hydrolysis of the ester groups[10,11].

The aim of the present study was to apply resonance *Raman* spectroscopy to the iron(II) complexes of long aliphatic chain *bipy* derivatives, $Fe(LC_{12})_3Cl_2$ and $Fe(LC_{18})_3Cl_2$ 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[12].

Iron(II) complexes, $Fe(LC_{12})_3Cl_2$ and $Fe(LC_{18})_3Cl_2$ 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_2O_5. The purity of the complexes was checked by elemental analyses.

Calculated for $Fe(C_{34}H_{56}O_2N_2)_3Cl_2$: 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 $Fe(C_{46}H_{80}O_2N_2)_3Cl_2$: 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. 1 600 rpm)[13]. The 1 221 cm^{-1} band of chloroform was taken as an internal standard. The intensities of the *Raman* bands were determined by the triangulation method. Once the intensities were found relative to a band of the internal standard, they were corrected for the ν^4 dependence of the scattering effect, self-absorption, and photomultiplier response.

Visible and UV absorption spectra were run on a Hitachi spectrophotometer in $CHCl_3$ solutions.

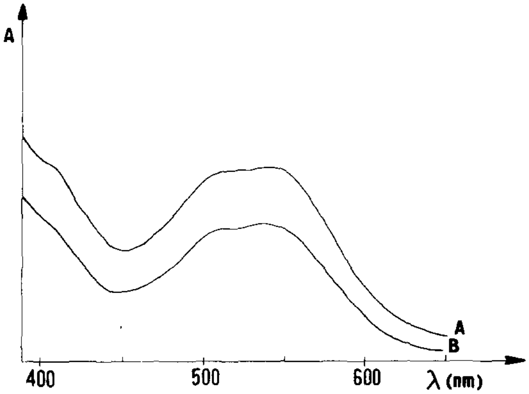

Fig. 1. Electronic absorption spectra of $Fe(LC_{12})_3Cl_2$ (A) and $Fe(LC_{18})_3Cl_2$ (B) in $CHCl_3$

Results and Discussion

The electronic absorption spectra of $Fe(LC_{12})_3Cl_2$ and $Fe(LC_{18})_3Cl_2$ (Fig. 1) show a strong band in the visible with a high energy shoulder. The main band appears at 18 500 cm^{-1} in both iron(II) complexes whereas the shoulder is observed at 19 600 and 19 500 cm^{-1} in LC_{12} and LC_{18} complexes, respectively. Thus, the positions of the main absorption and the shoulder are shifted to the red by 600 cm^{-1} and ca. 1 000 cm^{-1}, respectively, as compared with those observed in Fe(*bipy*)$_3^{2+}$ [5–7]. Moreover, the peak-to-shoulder separation amounts to 1 000–1 100 cm^{-1} in both iron complexes studied, whereas it equals ca. 1 600 cm^{-1} in the parent Fe(*bipy*)$_3^{2+}$ compound[5].

It follows from the far-infrared studies of LC_{12} and LC_{18} iron(II) complexes that the insertion of long-chained alkoxy group into 4,4′ positions of the *bipy* molecule does not affect the point symmetry (D_3) of the parent *bipy* complex[14]. If so, it would be reasonable to assign the main absorption to a $^1E \leftarrow {}^1A_1$ transition[15] while the shoulder on the high-frequency side can arise from either vibrational progressions[5, 6] or another CT transition[7, 16]. If the shoulder were of vibronic origin then the maxima of the excitation profiles should be a function of the wavenumber of the fundamental involved[1,2]. In such a case the wavenumber of the *Raman* band providing the greatest contribution to the electronic sideband is expected to be very close to peak-to-shoulder separation of ca. 1 100 cm^{-1}. On the other hand, if it is not the case, i.e. the sideband arises from another CT transition, the excitation profiles

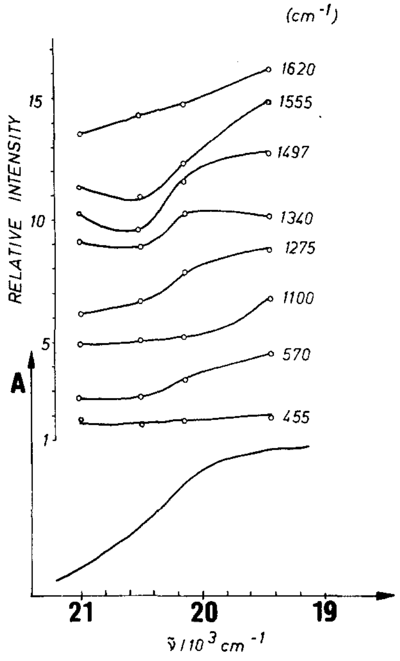

Fig. 2. Excitation profiles of $Fe(LC_{12})_3Cl_2$

should maximize at the same wavenumber (that of the electronic CT transition)[2]. As the exciting frequency approaches that of the shoulder some *Raman* bands of $Fe(LC_{12})_3Cl_2$ and $Fe(LC_{18})_3Cl_2$ exhibit considerable enhancement. Positions of these bands are listed in Table 1 along with depolarization ratios measured at 514.5 nm and tentative band assignments. Inspection of these data reveals that: (i) the pattern of the resonance *Raman* spectrum of either the LC_{12} or LC_{18} complex resembles that of $Fe(bipy)_3{}^{2+}$, i.e., the same normal modes are enhanced irrespective of the ligand type, (ii) the values of the depolarization ratio are somewhat higher than those expected for totally symmetric modes under resonance conditions[17] but there are no inversely polarized bands present.

Excitation profiles for Fe(LC_{12})$_3$Cl$_2$ and Fe(LC_{18})$_3$Cl$_2$ are displayed in Figs. 2 and 3. First of all, it should be noted that the positions of the excitation profiles maxima in the 19 500 cm^{-1} region of both compounds are not dependent upon the vibrational frequency. This result demonstrates that the electronic absorption at ca. 19 500 cm^{-1} is not a

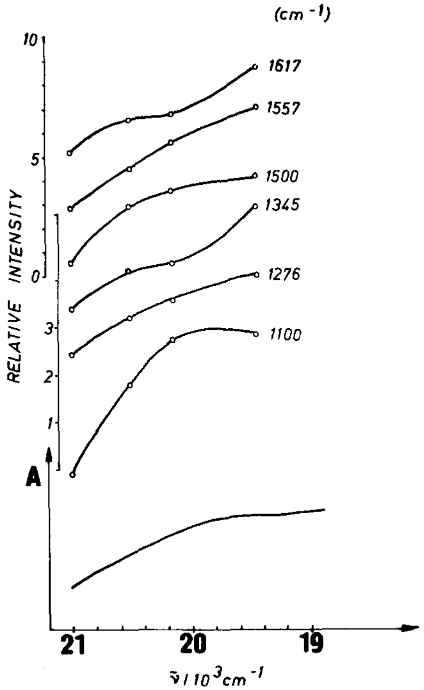

Fig. 3. Excitation profiles of Fe(LC_{18})$_3$Cl$_2$

vibronic sideband of the main visible absorption. In addition, it can be easily seen from Figs. 2 and 3 that the 1 100 cm^{-1} fundamental is not the one exhibiting the strongest enhancement. Among the bands observed in the R*R* spectra of Fe(LC_{12})$_3$Cl$_2$ those at 1 497, 1 555 and 1 620 cm^{-1} experience the most pronounced enhancement. Similarly, in the LC_{18} complex the bands appearing at 1 500, 1 557 and 1 617 cm^{-1} show the largest increase in intensity. The results of normal coordinate analysis of *bipy* and its Pd(II) complex[18, 19] have demonstrated that the bands found in the spectrum of *bipy* between 1 200 und 1 600 cm^{-1} arise from coupled C—N and C—C skeletal stretching vibrations. Other fundamentals present in the R*R* spectra of both LC_{12} and LC_{18} complexes are enhanced to a lesser extent.

Table 1. *Resonance Raman spectra of* $\mathrm{Fe}(LC_{12})_3\mathrm{Cl}_2$, $\mathrm{Fe}(LC_{18})_3\mathrm{Cl}_2$ *and their parent compound,* $\mathrm{Fe}(bipy)_3^{2+}$ [1] (cm^{-1})

$\mathrm{Fe}(bipy)_3^{2+}$		$\mathrm{Fe}(LC_{12})_3\mathrm{Cl}_2$		$\mathrm{Fe}(LC_{18})_3\mathrm{Cl}_2$		Assignment
ν	ρ_l	ν	ρ_l	ν	ρ_l	
1607	0.39	1620	0.54	1617	0.51	ν(C—N) + ν(C—C)
1563	0.40	1555	0.47	1557	0.49	ν(C—N) + ν(C—C)
1490	0.43	1497	0.38	1500	0.32	ν(C—N) + ν(C—C)
1321	0.39	1340	0.52	1345	0.47	ν(C—N) + ν(C—C)
1277	0.34	1275	0.46	1276	0.40	ν(C—C) + ν(C—N)
1173	0.36	[a]		[a]		
1109	p	1100	p	1102	p	ν(C—C) + ν(C—N)
1067	p	—		—		
1035	p	—		—		
1025	0.71	—		—		
768	0.26	—		—		
662	0.19	—		—		
642	dp	—		—		
—		570	p	566	p	δ(C—O—C)
—		455	p	461	p	δ(C—O—C)
370	0.22	—		—		

[a] partly overlapped by the 1221 cm^{-1} CHCl_3 band.
[p] polarized band.
[dp] depolarized band.

It is interesting to note that two new bands showing only fair resonance enhancement (cf. excitation profile plots) appear in the R*R* spectra of $\mathrm{Fe}(LC_{12})_3\mathrm{Cl}_2$ and $\mathrm{Fe}(LC_{18})_3\mathrm{Cl}_2$ complexes. They are located at 455, 570 cm^{-1} in the former complex and at 461, 566 cm^{-1} in the latter. Since these bands cannot result from symmetry alteration, it seems possible to assign them to ring deformations within C—O—C ring fragment.

According to theoretical treatment of *Raman* scattering[17] the values of depolarization ratio (ρ_l) for totally symmetric modes must approach the limiting value of 1/3 when the system is brought into resonance with incident frequency. This prediction holds when a single nondegenerate electronic state contributes to the total scattering intensity (A term enhancement). Higher ρ_l values observed for some bands in the R*R* spectra of $\mathrm{Fe}(LC_{12})_3\mathrm{Cl}_2$ and $\mathrm{Fe}(LC_{18})_3\mathrm{Cl}_2$ (Table 1) indicate that the B term (mixing two excited electronic states) also contributes to the scattering intensity. In such a case the resonance enhancement is no longer restricted to totally symmetric modes but also involves the vibrations having any symmetry which is contained in the direct product of the representations of the two electronic states.

In conclusion, it follows from the presented experimental data that the shoulder on the high-frequency side of the main visible absorption in $\mathrm{Fe}(LC_{12})_3\mathrm{Cl}_2$ and $\mathrm{Fe}(LC_{18})_3\mathrm{Cl}_2$ arises rather from separate electronic CT transition than the vibrational progressions.

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