eV), compared with that of **1**; Q = Cp (6.74 eV), is therefore consistent with the assigned π-acidity order of the ligands ($C_5H_5 > C_5Me_5$). This π-acidity order could perhaps account for the significantly greater abundance of dipositive ions in the mass spectrum of the permethylated analogue.

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Registry No. **1** (Q = C_5Me_5), 37299-12-0; **1** (Q = Cp), 54667-87-7; **2**, 12154-95-9; **3**, 12170-92-2.

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Resonance Raman Spectra and Excitation Profiles of Tris(α-diimine) Complexes of Iron(II)

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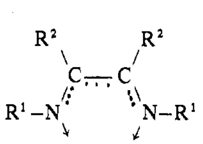
Measurements of the excitation profiles of six bands of the $[Fe(bmi)_3]^{2+}$ ion, eight bands of the $[Fe(bpy)_3]^{2+}$ ion, and thirteen bands of the $[Fe(phen)_3]^{2+}$ ion in aqueous solution have indicated that the shoulder on the high-frequency side of the main electronic bands of these ions in the visible region is a vibronic side band. For the first ion, the principal fundamental involved is that at 1400 cm^{-1}, for the second ion that at 1607 cm^{-1}, and for the third ion that at 1635 cm^{-1}. The resonance Raman spectra of the ions are dominated by bands arising from totally symmetric fundamentals and this indicates that only one electronic transition (the resonant one) is primarily responsible for the intensity of the Raman emission from these ions with excitation lines in the visible region.

Introduction

All α-diimine ligands can be represented by the general formula



where R^1 and R^2 may be H, alkyl, or phenyl groups. These substituents can also be connected, e.g., in the cases of 2,2′-bipyridyl and 1,10-phenanthroline. The ligands form tris complexes with iron(II) which are characterized by their high stability and intense absorption in the visible region.[1] The complex ions of iron(II) which are the subject of this investigation are those of the ligands 2,2′-bipyridyl, 1,10-phenanthroline, and biacetyl bis(N-methylimine), viz. $[Fe(bpy)_3]^{2+}$, $[Fe(phen)_3]^{2+}$, and $[Fe(bmi)_3]^{2+}$. The visible absorption spectra of these three ions have been extensively studied and the values of λ_{max} and ϵ_{max} for the main peaks are given in Table I.

Table I. Electronic Absorption Maxima of α-Diimineiron(II) Complexes[1]

Complex	λ_{max}/nm	$\tilde{\nu}_{max}/cm^{-1}$	$10^{-3}\epsilon_{max}/(dm^3\ mol^{-1}\ cm^{-1})$
$[Fe(bpy)_3]^{2+}$	524	19 100	8.7
$[Fe(phen)_3]^{2+}$	510	19 600	11.5
$[Fe(bmi)_3]^{2+}$	568	17 600	10.7

While it is generally agreed that the strong visible absorption arises from an electronic dipole allowed metal (3d) to ligand (π) charge-transfer transition,[2] what is not certain is whether the unresolved structure on the high-frequency side of the main absorption band (see Figures 5–9) arises from a vibration in an excited state or from other CT transitions. Under D_3 symmetry the degeneracy of the Fe^{2+} d orbitals and the ligand π orbitals is split[3] and there is thus the possibility of $^1E \leftarrow {}^1A_1$ or $^1A_2 \leftarrow {}^1A_1$ transitions. MO calculations have been performed for all systems[4–7] and in every case but one[7] indicate that only a single transition of the type $^1E \leftarrow {}^1A_1$ should contribute significantly to the absorption spectrum in the visible region. It was therefore proposed that the unresolved structure in the shoulder was mainly due to vibrational progressions[4–8] with only small contributions from other CT transitions. The positions and oscillator strengths of these additional transitions vary widely from paper to paper and due to the uncertainty in the frequency and intensity of the vibrational progression, if any, it is difficult to decide which analysis is most accurate.

Single-crystal polarized absorption studies[9] on the compound $[Fe(bpy)_3]SO_4$ have also shown that the main absorption band and the shoulder arose almost entirely from $^1E \leftarrow {}^1A_1$ transitions. The results of low-temperature studies on the absorption spectra of compounds containing the $[Fe(bpy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ ions suggest that the wavenumbers of the

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fundamentals responsible for the shoulders are 1600[9] and 1500 cm^{-1},[8] respectively, and hence are probably due to $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ vibrations. Earlier Krumholz[10] had performed a Gaussian analysis on the absorption spectrum of the $[\mathrm{Fe(bmi)_3}]^{2+}$ ion which led him to believe that there was a vibrational progression involving a fundamental whose wavenumber was ~1500 cm^{-1}. Recently, however, he (in collaboration with Serra and de Paoli[11]) reassigned the unresolved structure in the absorption spectrum of this ion to other CT transitions. This reassignment was partly based on a new curve analysis and also on the variation in the form of the spectrum as the substituents R^1 and R^2 were varied.

The aim of the present study was to apply resonance Raman (RR) spectroscopy to these tris(α-diimine) systems in the hope of resolving the ambiguities in the assignments of the absorption bands. As the incident frequency approaches that of a given allowed electronic transition, those normal modes which are vibronically active in that electronic transition should exhibit particularly striking enhancement of their Raman intensities.[12] If the unresolved structure in the electronic spectrum were vibronic in origin, one would expect the frequency of the mode whose Raman intensity showed the greatest enhancement to correspond closely to the peak-to-shoulder separation. The correspondence between the frequency and the separation is unlikely to be exact given the uncertainty in the estimates of the separations and also the possibility that more than one mode may be involved. The behavior of the depolarization ratios of the Raman bands as well as the type of mode enhanced (totally symmetric or nontotally symmetric) will also allow deductions to be made concerning the nature of the electronic absorption bands.

Experimental Section

Compounds. $[\mathrm{Fe(bmi)_3}]\mathrm{I_2{\cdot}3H_2O}$ and $[\mathrm{Fe(bpy)_3}]\mathrm{I_2{\cdot}5H_2O}$ were prepared according to literature methods.[1,13] $[\mathrm{Fe(phen)_3}]\mathrm{SO_4{\cdot}7H_2O}$ was purchased from G. F. Smith Co., Columbus, Ohio.

Spectral Measurements. The Raman spectra were measured as 10^{-2}–10^{-3} M solutions of the α-diimine complexes in 1 M sodium sulfate (internal standard) using the rotating-cell technique.[14,15] The spectra were recorded on a Spex Model 1401 double monochromator at each institution. Exciting lines at University College London were provided by Coherent Radiation Model 52 Ar$^+$ (514.5, 501.78 496.5, 488.0, 476.5, and 457.9 nm) and Model 52 Kr$^+$ (647.1, 568.2, 530.8, and 520.8 nm) lasers and by a Coherent Radiation Model 490 dye laser employing rhodamine 6G (586.1, 605.0, 601.4, and 621.5 nm). These results were checked at Marquette University by using a Spectra-Physics Model 164 Ar$^+$ laser and a Spectra-Physics Model 375 CW dye laser employing rhodamine 6G (580–630 nm) or sodium fluorescein (535–575 nm). Intensities were measured relative to the 981-cm^{-1} $\nu_1(a_1)$ band of the $\mathrm{SO_4}^{2-}$ ion. Peak areas were determined by the trace-and-weigh technique (University College London) and by direct integration using a planimeter (Marquette University).

Results and Discussion

The wavenumbers of the Raman bands of the $[\mathrm{Fe(bpy)_3}]^{2+}$, $[\mathrm{Fe(phen)_3}]^{2+}$, and $[\mathrm{Fe(bmi)_3}]^{2+}$ ions in aqueous solutions are given in Table II, together with depolarization ratios measured either with resonant (in the case of totally symmetric fundamentals) or nonresonant (in the case of nontotally symmetric fundamentals) excitation. As is seen in Figures 1–3, the Raman spectra of the complexes are strongly dependent on the exciting frequency used and are dominated by bands arising from the skeletal stretching vibrations of the ligands. This indicates in the cases of the bpy and phen complexes that the transferred electron is extensively delocalized over the aromatic ring system as predicted by Hanazaki and Nagakura.[5] Additionally for the $[\mathrm{Fe(bpy)_3}]^{2+}$ and $[\mathrm{Fe(phen)_3}]^{2+}$ ions a large number of bands were observed above 2000 cm^{-1} (Figure 4) which can be attributed to overtones and combination bands. The wavenumbers and most probable assignments are shown in Table III.

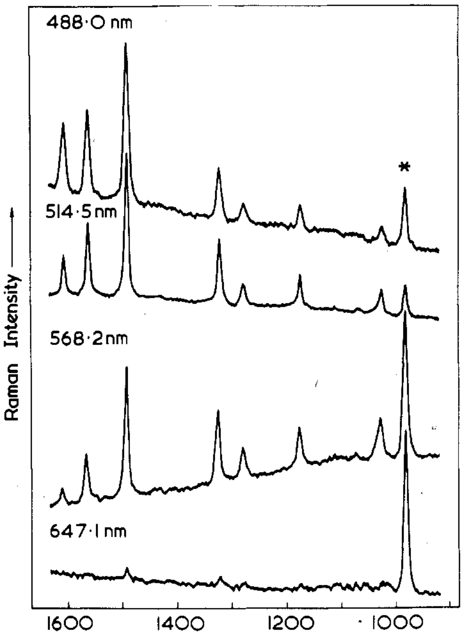

Figure 1. Raman spectrum of the $[\mathrm{Fe(bpy)_3}]^{2+}$ ion in the 1600–900-cm^{-1} region. Spectral slit width is 2–3 cm^{-1}; the asterisk indicates the 981-cm^{-1} reference band of the sulfate ion.

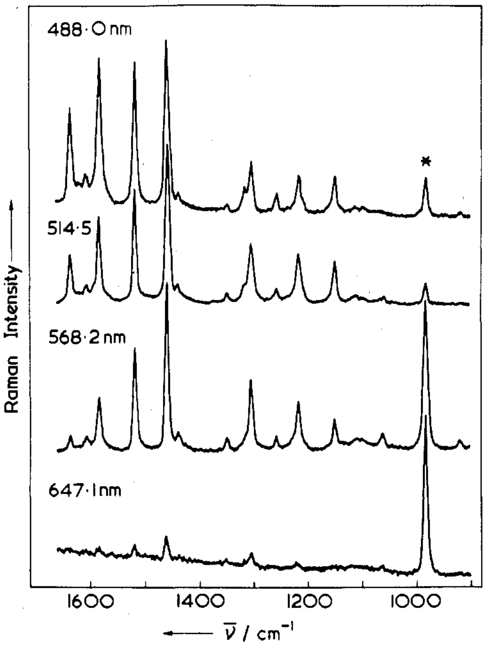

Figure 2. Raman spectrum of the $[\mathrm{Fe(phen)_3}]^{2+}$ ion in the 1600–900-cm^{-1} region. Spectral slit width is 2–3 cm^{-1}; the asterisk indicates the 981-cm^{-1} reference band of the sulfate ion.

Our observations lead us to conclude that any contribution to the absorption band by other CT transitions as proposed by Krumholz et al.[11] must be small since the RR spectra were dominated by bands arising from totally symmetric fundamentals (see Table II). The spectrum of the $[\mathrm{Fe(phen)_3}]^{2+}$ ion did show a few weak bands that were depolarized and this is significant as we shall show later. As stated before, the main electronic peak is definitely due to the $^1\mathrm{E} \leftarrow {}^1\mathrm{A}_1$ transition. If the unresolved shoulder were purely electronic in origin, it could only arise from $^1\mathrm{E} \leftarrow {}^1\mathrm{A}_1$ and/or $^1\mathrm{A}_2 \leftarrow {}^1\mathrm{A}_1$ transitions.[3] Under these conditions nontotally as well as totally symmetric modes would be enhanced as the systems are brought into resonance by varying the frequency of the exciting

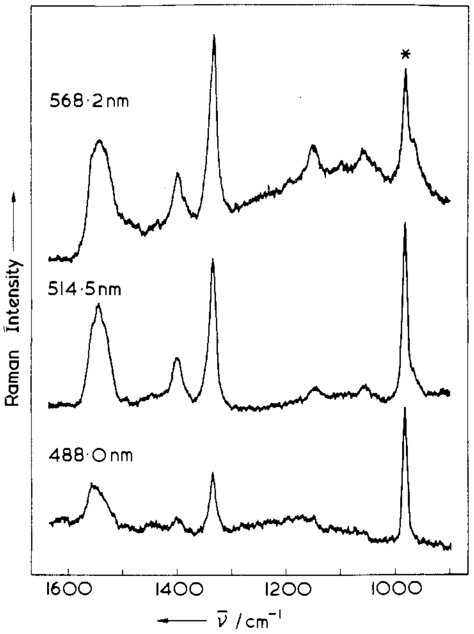

Figure 3. Raman spectrum of the $[Fe(bmi)_3]^{2+}$ ion in the 1600-900-cm^{-1} region. Spectral slit width is 2-3 cm^{-1}; the asterisk indicates the 981-cm^{-1} reference band of the sulfate ion.

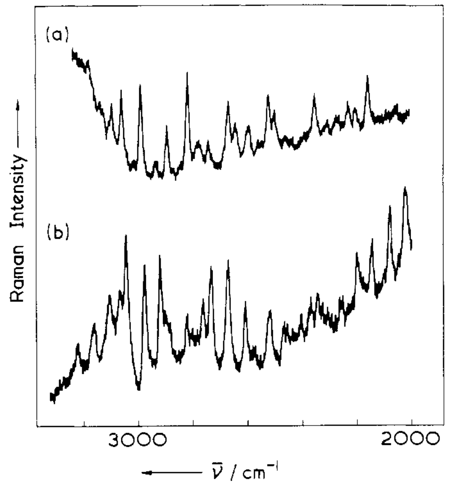

Figure 4. Raman spectra of (a) $[Fe(bpy)_3]^{2+}$ and (b) $[Fe(phen)_3]^{2+}$ in the 3200-2000-cm^{-1} region. Spectral slit width is 2-3 cm^{-1}.

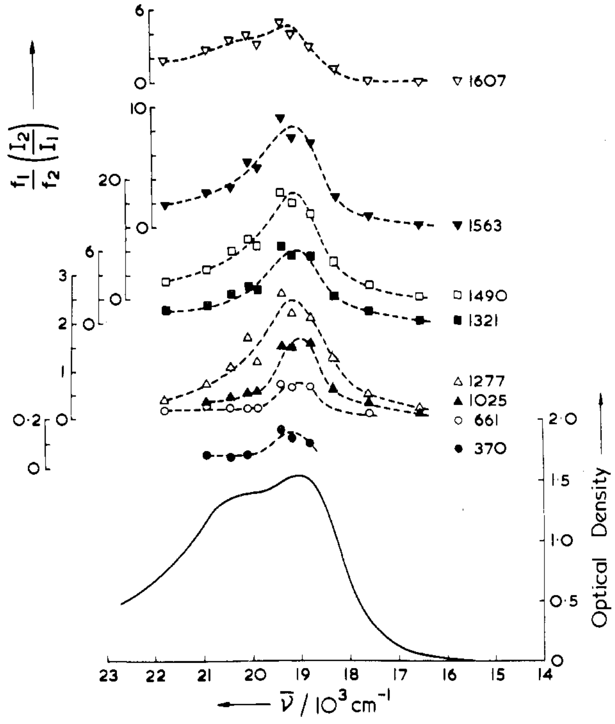

Figure 5. Excitation profiles of the $[Fe(bpy)_3]^{2+}$ ion in aqueous solution. Note that the ordinate scale for each fundamental may differ. I is the measured intensity; f is the ν^4 correction factor.

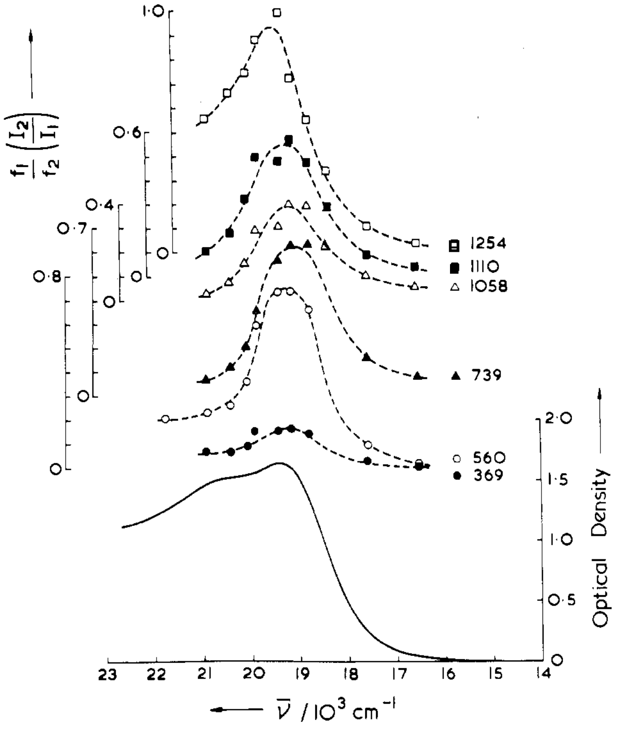

Figure 6. Excitation profiles of the $[Fe(phen)_3]^{2+}$ ion in aqueous solution (1254-369 cm^{-1}).

line. This must be true as can be seen by considering the B part of Albrecht's expression[12] for $(\alpha_{\rho\sigma})_{ij}$ which in turn determines the intensity of a particular vibrational mode. The magnitude of B and thus the intensity of the band are strongly dependent on a coupling term of the form $\langle e|h_a|s\rangle$ where e and s refer to any two excited electronic states of a molecule while h_a is a coupling operator which takes the symmetry of the ath normal mode. A coupling term of the type $\langle E|h_a|E\rangle$ would be finite for a_1, a_2, and e modes whereas if the type was $\langle E|h_a|A_2\rangle$, only e modes would give a nonzero value. Since we did not observe any inverse-polarized (a_2) bands on resonance nor resonance enhancement of any depolarized modes, we can assume that the oscillator strengths of any other electronic transitions present are too small to account for the shoulder on the main absorption band.

The depolarization ratios of all bands remained constant, within experimental error, except for the 1300- and 1313-cm^{-1} bands of the $[Fe(phen)_3]^{2+}$ ion whose values increased monotonically from 0.34 to 0.52 and from 0.44 to 0.72, respectively, as the exciting frequency varied from 514.5 to 457.9 nm. This observation, together with the few depolarized bands observed in its Raman spectrum, suggests the presence of another interacting CT transition[15-17] at higher energy. Indeed the intensity of the absorption spectrum of the $[Fe(phen)_3]^{2+}$ ion does not decrease at high frequency (see Figures 6 and 7) as do those of the other α-diimine complexes.

In order to determine which Raman bands showed the greatest enhancement we made detailed measurements of the intensities of many bands of each complex ion, relative to an

Table II. Resonance Raman Spectra of Iron(II)-α-Diimine Complexes in Aqueous Solution

$[Fe(bpy)_3]^{2+\,a}$			$[Fe(phen)_3]^{2+\,a}$			$[Fe(bmi)_3]^{2+\,b}$		
$\tilde{\nu}$/cm^{-1}	ρ	Intens	$\tilde{\nu}$/cm^{-1}	ρ	Intens	$\tilde{\nu}$/cm^{-1}	ρ	Intens
146 ± 0.8	p	w	144 ± 0.5	0.13	m	317 ± 0.5	0.16	w
370 ± 0.5	0.22	w	150 ± 0.5			405 ± 0.6	0.42	w
642 ± 0.9	dp	vw	197 ± 0.5	0.64	w	479 ± 0.5	0.21	m
662 ± 0.5	0.19	m	313 ± 0.5	0.11	w	769 ± 0.5	0.18	w
768 ± 0.5	0.26	w	369 ± 0.7	0.75	w	967 ± 1	0.49	mw
1025 ± 1	0.71	m	433 ± 0.6	0.43	w	1057 ± 1	0.23	w
1035 ± 1	p	mw	464 ± 1.4	p?	vw	1150 ± 1	0.10	w
1067 ± 1	p	w	493 ± 0.5	0.58	w	1334 ± 1	0.45	s
1109 ± 1	p	mw	560 ± 0.5	0.21	m	1400 ± 1	0.50	m
1173 ± 1	0.36	ms	647 ± 1	dp	vw	1542 ± 1	0.44	s
1277 ± 1	0.34	m	727 ± 1	dp	vw	1555 ± 1	0.10	w
1321 ± 1	0.39	s	739 ± 1	0.46	mw			
1490 ± 1	0.43	vs	880 ± 1	0.17	mw			
1563 ± 1	0.40	s	915 ± 1	dp	vw			
1607 ± 1	0.39	ms	1058 ± 1	0.17	w			
			1094 ± 1	0.69	w			
			1110 ± 1	0.25	w			
			1146 ± 1	0.42	m			
			1213 ± 1	0.35	m			
			1254 ± 1	0.68	mw			
			1300 ± 1	0.34	m			
			1313 ± 1	0.44	w			
			1346 ± 1	0.14	mw			
			1436 ± 1	0.27	w			
			1458 ± 1	0.30	vs			
			1517 ± 1	0.38	vs			
			1582 ± 1	0.40	s			
			1606 ± 1	0.54	mw			
			1618 ± 1	dp?	w			
			1635 ± 1	0.26	m			

[a] Measured using 514.5-nm (polarized bands) or 647.1-nm (depolarized bands) excitation. [b] Measured using 568.2-nm excitation.

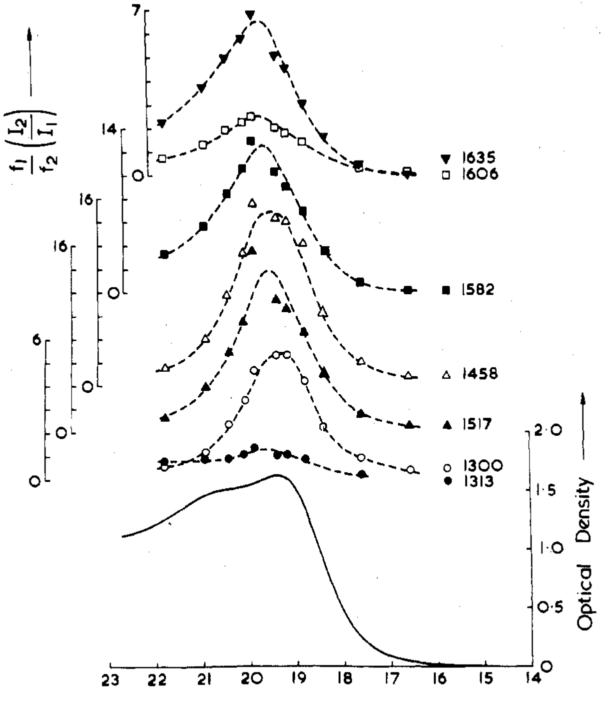

Figure 7. Excitation profiles of the $[Fe(phen)_3]^{2+}$ ion in aqueous solution (1635–1300 cm^{-1}).

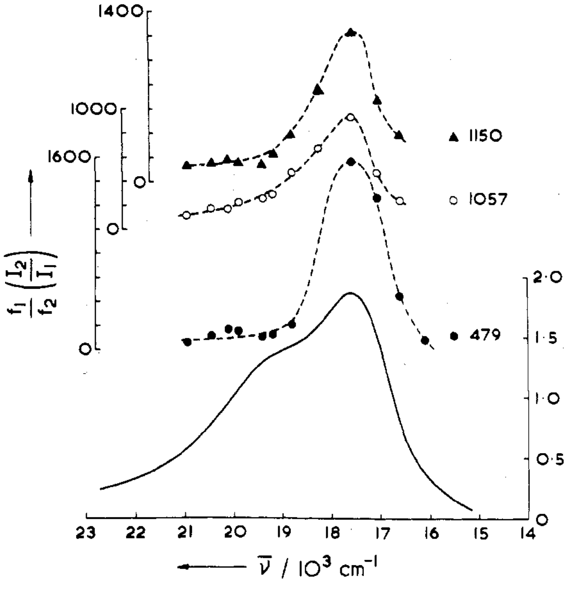

Figure 8. Excitation profiles of the $[Fe(bmi)_3]^{2+}$ ion in aqueous solution (1150–479 cm^{-1}).

internal standard. The resulting curves (excitation profiles) are displayed in Figures 5–9. The relative intensities are considered to be correct within ±10% and error bars have been omitted purely for the sake of clarity. For the $[Fe(bpy)_3]^{2+}$ ion (Figure 5) the bands at 1490, 1563, and 1607 cm^{-1} show the greatest enhancement. Taking the intensity of each band to be unity at 605 nm, it becomes 26, 37, and 39, respectively, at the absorption band maximum ($\nu_{0,0} \approx 19\,100$ cm^{-1}) and 12, 15, and 30, respectively, in the $\nu_{1,0}$ region (taking the intensity of the Raman bands induced by 488.0-nm excitation as an approximation). Hence the 1607-cm^{-1} band provides the greatest contribution to the electronic side band and its frequency corresponds very well with the peak-to-shoulder separation of 1600 cm^{-1} measured by Palmer and Piper.[9] It is worth noting that, although this band shows the greatest enhancement, it is not the most intense band in the resonance Raman spectrum (see Figure 1).

In the case of the $[Fe(phen)_3]^{2+}$ ion (Figures 6 and 7) there is no question that the band at 1635 cm^{-1} shows the greatest

Table III. Frequencies of Overtone and Combination Bands for the $[Fe(bpy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ Ions in Aqueous Solution[a]

$[Fe(bpy)_3]^{2+}$		$[Fe(phen)_3]^{2+}$	
$\tilde{\nu}/cm^{-1}$	Assignment, cm^{-1}	$\tilde{\nu}/cm^{-1}$	Assignment, cm^{-1}
2152	1490 + 662	2014	1458 + 560
2196	1173 + 1025	2072	1517 + 560
2225	1563 + 662	2138	1582 + 560
2270	1607 + 662	2164	1606 + 560
2303	1277 + 1025	2193	1635 + 560
2347	1321 + 1025/2 × 1173	2222	2 × 1110
2440	1277 + 1173	2252	1517 + 739
2494	1321 + 1173	2302	2 × 1146?
2514	1490 + 1025	2334	1458 + 880
2590	1321 + 1277/1563 + 1025	2357	1300 + 1058/1213 + 1146
2637	1607 + 1025/2 × 1321	2376	1635 + 739
2665	1490 + 1173	2393	1517 + 880
2731	1563 + 1173	2456	1582 + 880
2765	1490 + 1277	2512	1635 + 880
2778	1607 + 1173	2564	1517 + 1058?
2809	1490 + 1321	2602	2 × 1300
2840	1563 + 1277	2664	1458 + 1213
2885	1563 + 1321/1607 + 1277	2727	1517 + 1213
		2753	1458 + 1300
2927	1607 + 1321	2790	1582 + 1213
2980	2 × 1490	2813	1517 + 1300
3052	1563 + 1490	2875	1582 + 1300
3085	1607 + 1490?	2893	1458 + 1436
3127	2 × 1563	2911	2 × 1458
3171	1607 + 1563	2966	1517 + 1458
		3032	2 × 1517
		3057	1606 + 1458
		3095	1635 + 1458/1582 + 1517
		3151	1635 + 1517
		3213	2 × 1606
		3235	1635 + 1606

[a] Accurate to ±2 cm^{-1} for sharp bands.

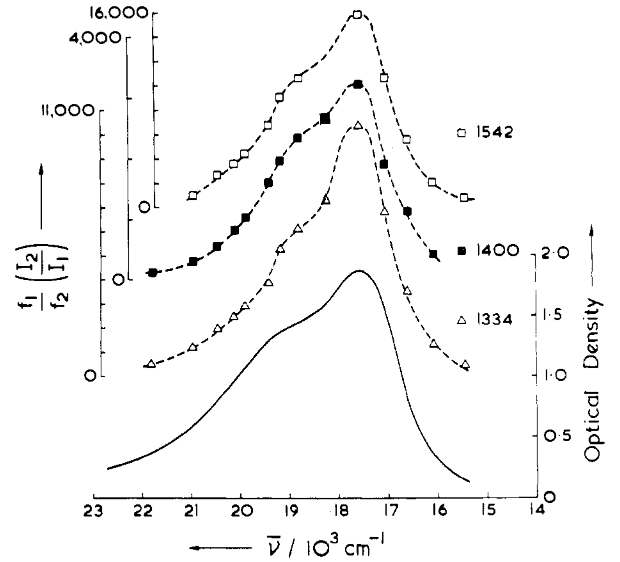

Figure 9. Excitation profiles of the $[Fe(bmi)_3]^{2+}$ ion in aqueous solution (1542–1334 cm^{-1}).

enhancement. Taking its intensity at 605 nm to be unity, it becomes 200 at the frequency of the absorption band maximum ($\nu_{0,0}$) and 170 at the high-frequency shoulder ($\nu_{1,0}$), i.e., more than 3 times that of any other band, although the 1582- and 1606-cm^{-1} bands also experience strong enhancement. The comparison of the peak-to-shoulder separation in the absorption band (1500 cm^{-1} [8]) with the frequency of the most strongly enhanced band (1635 cm^{-1}) is not as good in this case. However, this is not entirely unexpected since as we stated previously other modes may also be involved.

Last, for the $[Fe(bmi)_3]^{2+}$ ion, the three bands at 1334, 1400, and 1542 cm^{-1} all show strong enhancement (Figures 8 and 9) but it is the intensity of the 1400-cm^{-1} band which increases the most on changing the frequency from off- to on-resonance values. Taking the intensity of each band to be unity at 647.1 nm, it becomes 21, 32, and 22, respectively, at the absorption band maximum, and 12, 22, and 13, respectively, at the shoulder. The frequency difference between the maximum and the shoulder of the excitation profile of each of these three bands is quite close to one vibrational quantum of the specified bands in each case. The agreement between the frequency of the most strongly enhanced band (1400 cm^{-1}) and the peak-to-shoulder separation in the absorption spectrum ($\sim$1500 cm^{-1} [10]) is quite reasonable.

Finally, our measurements show that the wavenumber of the mode primarily responsible for the vibronically induced side bands increases in the order bmi (1400) < bpy (1607) < phen (1635 cm^{-1}). It has been generally assumed that this mode is largely attributable to the C$\stackrel{...}{-}$N stretching mode,[5,10] and the observed order given above is consistent with this view since a fairly large change would be expected in ν(C$\stackrel{...}{-}$N) on going from the aliphatic bmi to the aromatic bpy, and a smaller increase would be expected when bpy is replaced by phen.

Conclusion

Measurement of the excitation profiles for various bands of the $[Fe(bmi)_3]^{2+}$, $[Fe(bpy)_3]^{2+}$, and $[Fe(phen)_3]^{2+}$ ions in aqueous solution has demonstrated that the shoulders at approximately 19 100, 20 500, and 21 000 cm^{-1}, respectively, on the high-frequency side of the main electronic bands of these ions in the visible region are largely due to vibronic transitions. For the $[Fe(bmi)_3]^{2+}$ ion the principal fundamental involved is that giving rise to the Raman band at 1400 cm^{-1} (cf. Krumholz's original proposal[1] of about 1500–1600 cm^{-1}), for the $[Fe(bpy)_3]^{2+}$ ion it is that giving rise to the Raman band at 1607 cm^{-1} (cf. a value of 1600 cm^{-1} suggested by low-temperature polarized crystal spectra[9]), and for the $[Fe(phen)_3]^{2+}$ ion it is that giving rise to the Raman band at 1635 cm^{-1} (cf. a value of 1500 cm^{-1} suggested by Day and Sanders[8]). In all cases other fundamentals are also involved but to a lesser extent. The domination of the resonance Raman spectra of the complex ions by bands arising from totally symmetric fundamentals has shown that only one electronic transition ($^1E \leftarrow {}^1A_1$) contributes to the absorption in the visible region.

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Registry No. $[Fe(bpy)_3]^{2+}$, 15025-74-8; $[Fe(phen)_3]^{2+}$, 14708-99-7; $[Fe(bmi)_3]^{2+}$, 20498-13-9.

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Localized and Internuclear Carbonyl Scrambling in Azulenepentacarbonyldiiron(*Fe–Fe*) and Its Ruthenium Analogue

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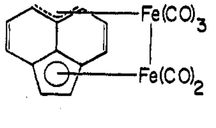
The molecules $(C_{10}H_8)Fe_2(CO)_5$ and $(C_{10}H_8)Ru_2(CO)_5$ have been shown to be fluxional by carbon-13 NMR. The slow-exchange spectrum for each molecule consists of five distinct carbonyl resonances. This is consistent with the crystallographically determined structure of $(C_{10}H_8)Fe_2(CO)_5$. On the basis of its NMR spectrum at −90 °C $(C_{10}H_8)Ru_2(CO)_5$ is assigned the same gross structure. Between −125 and −16 °C for the iron compound and between −90 and 29 °C for the ruthenium compound, three distinct carbonyl resonances of the $M(CO)_3$ groups are seen to collapse and form a single peak. From line shape analysis the activation energies for these processes are $E_a = 9.7 \pm 0.6$ and 11.5 ± 0.7 kcal mol^{-1} for the iron and ruthenium compounds, respectively, assuming $A = 10^{13.2}$ in each case. At higher temperatures all five carbonyl groups are observed to scramble. The observed line shape changes are well reproduced by calculated spectra based on a random-exchange matrix. Activation energies (again assuming $A = 10^{13.2}$) for these processes are $E_a = 15.4 \pm 1.0$ and 18.3 ± 1.1 kcal mol^{-1} for the iron and ruthenium compounds, respectively.

Introduction

Following our early studies of carbonyl scrambling in binuclear complexes of the type in which polyolefin ligands attached to the metal atoms were separate and unconnected for the two metal atoms, e.g., $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ and its derivatives[1–5] and $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5(CNCH_3)$,[5,6] we have examined some systems in which each metal atom is attached to a different portion of one large polyolefin. A few that we have published include **1**,[7] **2**,[7], **3**,[8] **4**,[9] **5**,[9] and **6**.[10]



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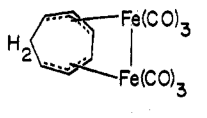

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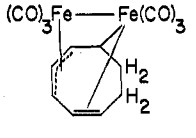

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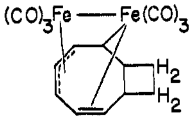

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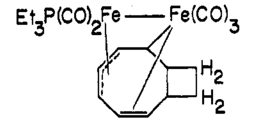

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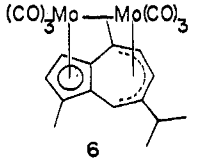

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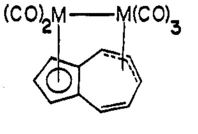

M = Fe 7
Ru 8

In the compounds with separate olefinic ligands on each metal atom mentioned above,[1–6] as well as $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$,[11] the characteristic process is *inter*nuclear exchange of CO groups; CO groups pass from one metal atom to the other, with bridged structures providing a low-energy pathway. Thus far, our studies of molecules with both metal atoms attached to the same large relatively rigid polyolefin have failed to reveal any indication of such *inter*nuclear exchange. For compounds **1** and **3–6**, the experimental results positively rule out the possibility of internuclear exchange. For structure **2**, the observations do not exclude it, but they can be fully and satisfactorily explained by assuming only local averaging, that is, scrambling of CO groups within each of the individual $Fe(CO)_3$ groups.

We report here the occurrence of internuclear scrambling in the case of (azulene)$Fe_2(CO)_5$ (**7**) and (azulene)$Ru_2(CO)_5$ (**8**). The structure of the iron compound was determined x-ray crystallographically some years ago by Churchill.[12]

Experimental Section

All samples were handled under nitrogen. Hexane and toluene were dried over Na–K alloy and distilled prior to use. CH_2Cl_2 was stored over molecular sieves and purged with nitrogen before use. Infrared spectra were recorded on a Perkin-Elmer 467 spectrometer. Carbon-13 NMR spectra were recorded on a Jeol-100/Nicolet 1080 FT system at 25.0352 MHz.

Azulenepentacarbonyldiiron, **7**, was prepared by reacting azulene (0.5 g, 3.9 mmol) with $Fe_2(CO)_9$ (3.6 g, 10 mmol) in 50 ml of hexane at room temperature for 40 h. After removal of the solvent at low pressure the residue was extracted with 1:1 CH_2Cl_2–hexane. Chromatography on 100–200 mesh Florisil using 1:1 CH_2Cl_2–hexane as eluent yielded **7** as a dark red band. The solution was concentrated and crystallized at −30 °C. The compound was identified by its IR spectrum in CS_2 (carbonyl bands at 2040, 1990, and 1970 cm^{-1}) and by the unit cell dimensions obtained for a single crystal, $a = 7.37$ Å, $b = 14.51$ Å, $c = 14.83$ Å, $\alpha = 116.0°$, $\beta = 92.9°$, and $\gamma = 92.2°$. These data agree with values previously reported in the literature.[12,13]

Attempts to prepare azulenepentacarbonyldiruthenium, **8**, by a literature procedure[14] in heptane yielded only $Ru_3(CO)_7(C_{10}H_8)$, as identified by IR spectroscopy. When toluene was used as the solvent, satisfactory yields of $(C_{10}H_8)Ru_2(CO)_5$ were obtained. Azulene (0.25 g, 1.95 mmol) and $Ru_3(CO)_{12}$ (0.5 g, 0.782 mmol) were refluxed in 250 ml of toluene for 24 h. After removal of solvent at low pressure, excess azulene was recovered by sublimation at room temperature and 10^{-3} Torr. The residue was extracted with CH_2Cl_2 and chromatographed on a 30 × 1.5 cm column packed with alumina, activity grade III, and using 1:4 CH_2Cl_2–hexane as eluent. The yellow band