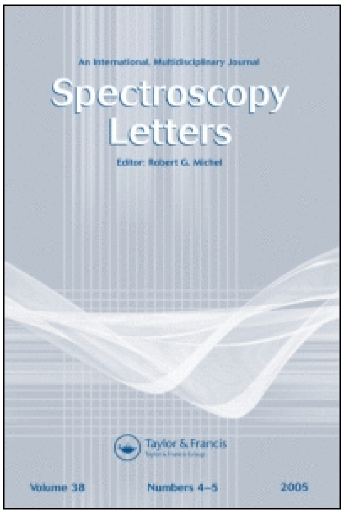

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Electronic and Resonance Raman Spectra of a Multibridged Iron Porphyrin

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To cite this Article Araki, Koiti , Santos, Paulo S. and Toma, Henrique E.(1993) 'Electronic and Resonance Raman Spectra of a Multibridged Iron Porphyrin', Spectroscopy Letters, 26: 8, 1417 — 1426
To link to this Article: DOI: 10.1080/00387019308011619
URL: http://dx.doi.org/10.1080/00387019308011619

SPECTROSCOPY LETTERS, 26(8), 1417-1426 (1993)

ELECTRONIC AND RESONANCE RAMAN SPECTRA OF A MULTIBRIDGED IRON PORPHYRIN

Key words: Resonance Raman spectra, iron porphyrin, multibridged porphyrin

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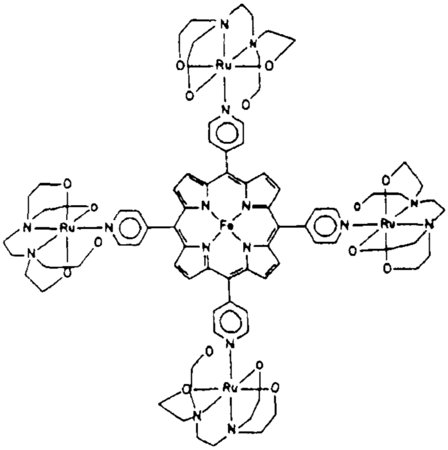
ABSTRACT

Reported are the electronic and resonance Raman (rR) spectra of a multibridged iron porphyrin derived from meso-tetra(4-pyridil)porphynate iron(II) by complexing the pyridine residues with $[Ru^{II}(edta)]^{2-}$ ions. The polymetallated system exhibits the characteristic Soret band at 428 nm (log ε = 5.2) and a shoulder around 465 nm (4.6). The rR enhancement of the porphyrin vibrational modes is similar to those previously reported for typical porphyrins; however, an additional feature appears around 465 nm, associated with the selective enhancement of some pyridine vibrational modes. Based on the rR excitation profiles the absorption band at 465 nm was assigned to a Ru^{II}-to-pyridine $d_{\pi} \rightarrow p_{\pi}*$ charge-transfer transition.

INTRODUCTION

In a previous paper we reported[1,2] the synthesis and electrochemical characterization of a new multibridged iron porphyrin derived from meso-tetra(4-pyridil)porphynate iron chloride, [Fe(TPyP)Cl], by complexing the pyridine residues with $[Ru(edta)]^-$ ions.



This modified porphyrin is of great interest in multielectron and photoredox catalysis because of the possibility of exploring the cooperative electronic interactions between the central and peripheral metal complexes.[1-7] In order to obtain relevant information on this type of interaction, we investigated the electronic and the resonance Raman spectra of the multibridged porphyrin in aqueous solution.

EXPERIMENTAL

The multibridged $Na_4[Fe(TPyP)Cl\{Ru(edta)\}_4].17H_2O$ complex was synthesized from [Fe(TPyP)Cl] and $[Ru(Hedta)(H_2O)]$ as previously reported,[1] and characterized by means of micro-analysis, electronic spectroscopy and cyclic voltammetry. The reduced complex was generated electrochemically or by using zinc amalgam under an argon atmosphere, in the presence of 5 mM acetate buffer (pH 4.5). A small excess of $[Ru(edta)(H_2O)]^{2-}$ was employed in all experiments in order to prevent the dissociation of the complex. The $[Ru^{II}(edta)(isonicotinamide)]^-$ complex was generated in solution by reacting $[Ru(Hedta)(H_2O)]$ with four fold excess of isonicotinamide, in the presence of zinc amalgam.

The electronic spectra were recorded on a Hewlett-Packard model 8452A diode-array spectrophotometer. Resonance Raman spectra were obtained using a spinning cell, and a Jarrel-Ash model 25-300 Raman double-spectrometer equipped with Spectra Physics argon and kripton ion lasers. The measurements were carried out using a 0.05 mM aqueous solution of (1) in the presence of 0.2 M Na_2SO_4 or a 1.0 mM $[Ru^{II}(edta)(isonicotinamide)]^{2-}$ solution containing 1.00 M KNO_3. The peak intensities were measured by comparison with that of the sulphate Raman peak at 980 cm^{-1}.

RESULTS AND DISCUSSION

The $[Fe^{II}(TPyP)\{Ru^{II}(edta)\}_4]^{8-}$ complex (1) exhibits the Soret, β and α bands characteristic of the porphyrin ring at 428 (5.2), 546 (4.2) and 614 nm (4.1) respectively, and an additional shoulder at 465 nm, as shown in Figure 1.A. A similar absorption band has been observed for $[Ru^{II}(edta)L]^{2-}$ complexes containing substituted pyridine ligands,[8] e.g., isonicotinamide (Figure 2.A), and has been ascribed to a ruthenium-to-pyridine $d_\pi \rightarrow p_\pi^*$ charge-transfer transition.

The rR spectrum of the ruthenium(II)-isonicotinamide complex was obtained for comparison purposes, by direct excitation within the ruthenium(II)-

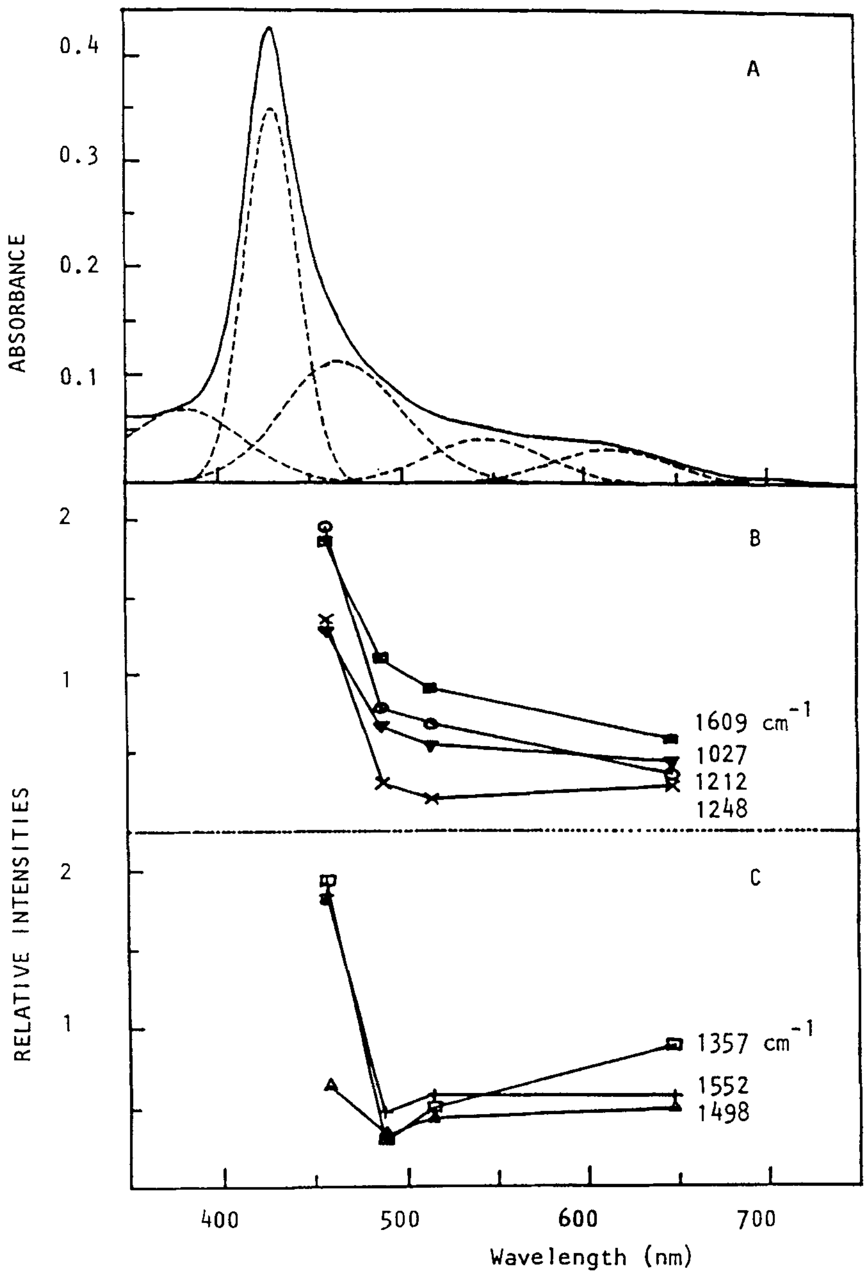


Fig. 1. (A) Deconvoluted electronic spectrum of the multibridged porphyrin (1) and typical resonance Raman excitation profiles for (B) pyridine and (C) porphyrin vibrational modes.

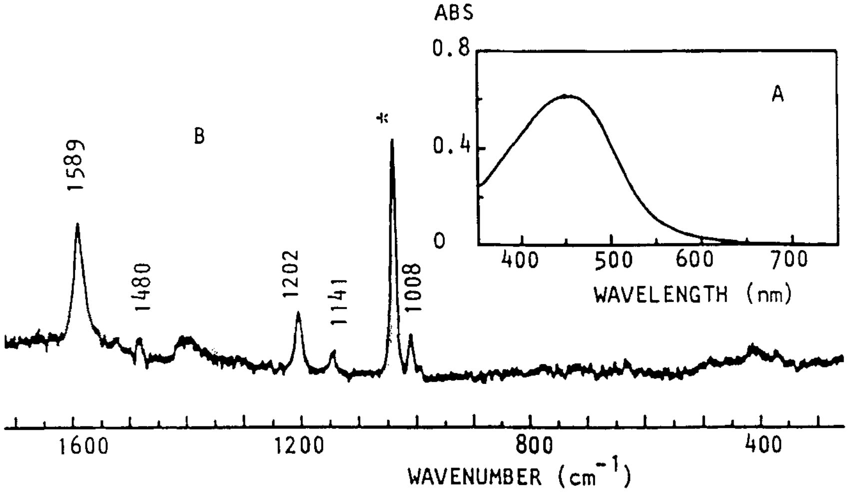


Fig. 2. (A) Electronic spectrum of the [Ru(edta)(isonicotinamide)]$^{2-}$ complex and (B) its corresponding resonance Raman spectrum in aqueous solution, λ_{exc} = 457 nm (* sulphate peak)

to-pyridine d$\pi \rightarrow$pπ^* charge transfer band, as shown in Figure 2.B. The spectrum exhibits strong and well resolved Raman peaks at 1589, 1202, 1141 and 1008 cm^{-1} associated with totally symmetric vibrational modes of the pyridine ring (Table 1).

Typical resonance Raman spectra of (1) using different excitation lines are shown in Figure 3. The Raman peaks at 1609, 1248, 1212 and 1027 cm^{-1} were ascribed to pyridine vibrational modes based on a previous assignment[9] for the [Fe^{III}(TMPyP)]$^{5+}$ complex. These wavenumbers are correlated with those observed for [Ru^{II}(edta)(isonicotinamide)]$^{2-}$ complex. The remaining frequencies

TABLE 1

Raman frequencies[a] for the multibridged porphyrin (1) and related species

$Fe^{III}TMPyP^{b}$	$Fe^{II}TMPyP^{c}$	$Ru^{II}(edta)(isonic)$	$Fe^{II}Ru^{II}$ (1)	Tentative Assignment
1641 m, p	1647 s	1589 vs	1609 s	ν(py)
1554 m, p	1547 vs		1552 s	$\nu(C_\beta$-$C_\beta)$
1518 vw, p		1480 vw	1530 vw	ν(py)
1495 s, dp			1498 w	$\nu(C_\beta$-$C_\beta)$
1448 s, p	1433 m		1450 vw	$\nu(C_\alpha$-$C_\beta)$
1361 s, p	1345 m		1357 s	$\nu(C_\alpha$-N)
1292 s, dp				$\nu(C_\alpha$-$C_\beta)$
1277 m, dp			1270 m	$\nu(C_\alpha$-N)
1254 w, p	1252 m		1248 m	$\nu(C_m$-py)
1220 m, p	1221 vs	1202 s	1212 s	ν(py)
1190 m, p	1194 s	1141 w		ν(py)
1104 m, dp				$\nu(C_\beta$-H)
1098 m, p	1097 w		1090 w	$\delta(C_\beta$-H)
1056 vw, p	1057 vw		1062 w	δ(C-H)py
1022 m, dp			1027 s	ν(py)
1010 w, p	1002 m	1008 m	1000 s	$\nu(C_\alpha$ -$C_m)$
905 w, p			900 vw	δ(porphyne)
886 w, dp				δ(porphyne)
823 m, dp			813 s	
793 w, p	795 m			ν(C-C) py
664 vw, p	664 w		668 w	
			485 s	δ(porphyne)
			435 s	δ(porphyne)
395 w, p	372 s		390 vs	δ(porphyne)
			324 m	δ(porphyne)
240 w, p				δ(porphyne)

a) w = weak, vw = very weak, m = medium, s = strong, vs = very strong,

p = polarized, dp = depolarized.

b) ref. 9, c) ref. 13

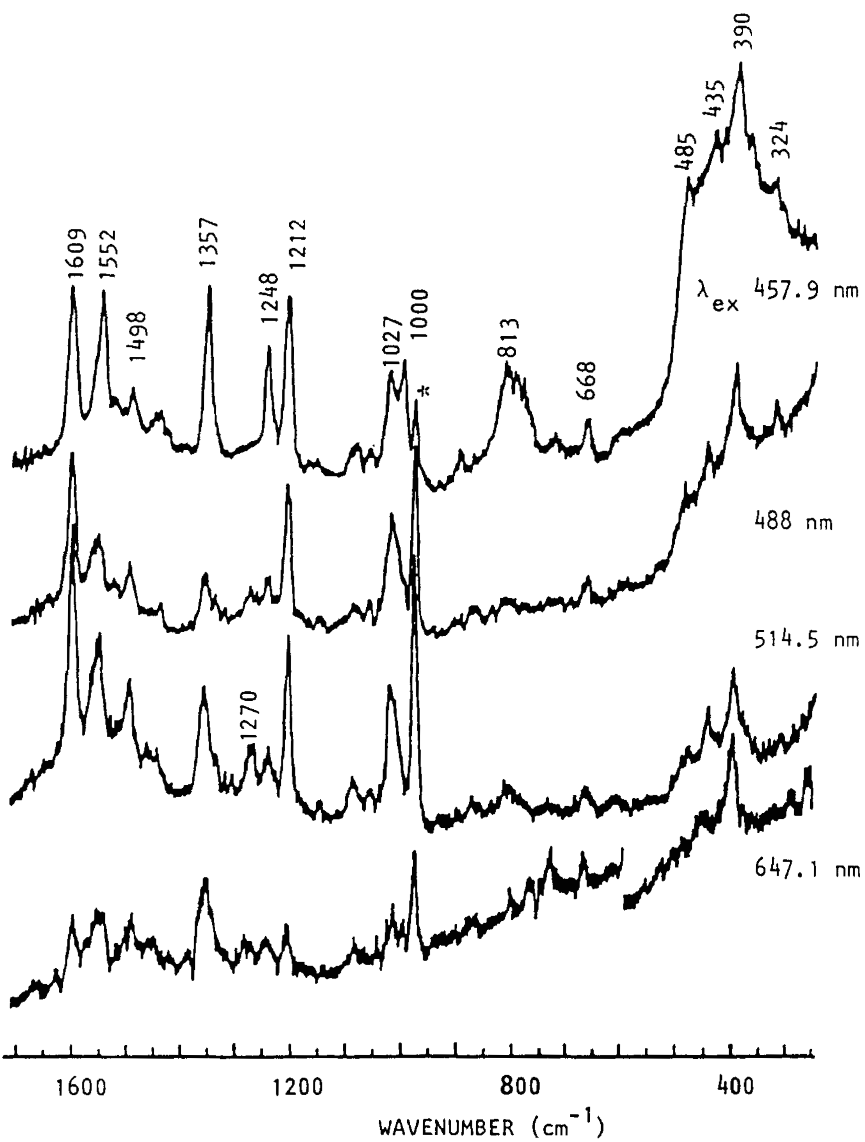


Fig. 3. Resonance Raman spectra of the multibridged porphyrin (1), in aqueous solution, at several excitation wavelengths (* sulphate peak).

follow very closely the general behavior previously reported[9] for the porphyrin vibrational modes.

According to the literature,[10-13] the $\nu(C_\beta\text{-}C_\beta)$, $\nu(C_\alpha\text{-}N)$ and the porphyrin core deformation frequencies are sensitive to the oxidation and spin states of the iron ion. These vibrational peaks are typically found at 1355-1369, 1560-1572 and 380-384 cm^{-1} for a low spin [Fe^{II}TPP] complex, while for a high spin complex they are usually found at 1341-1344, 1542-1554 and 372-376 cm^{-1}. The frequencies observed for (1), e. g. 1357, 1552 and 390 cm^{-1}, are consistent with a low spin configuration for the iron(II) ion. We suggest that the strong backbonding interactions from the [Ru^{II}edta]$^{2-}$ ions can increase the ligand field strength of the porphyne ring, leading to a low spin configuration, in contrast to the [FeTPP] and [FeTMPyP] species.

The rR excitation profiles for the multibridged porphyrin can be seen in Figure 1.B. The excitation at the Soret band is essentialy associated with Franck-Condon overlap factors (Albrecht, type A)[14] involving totally symetric A_{1g} vibrations. Raman enhancement by excitation at the α and β bands is governed by the Herzberg-Teller mechanism (type B)[14] involving A_{2g}, B_{1g} and B_{2g} modes, that couple the ground state with two excited states of suitable simmetries. In the last case the totally symmetric modes of the porphyrin ring are not strongly intensified, except in the case of meso-phenyl substituted porphyrins.[15] The vibrational modes of the pyridine groups of tetra(pyridil)porphyrins can also undergo rR enhancement by their coupling with the vibrations of the porphyne ring in the excited state. In porphyrins such as [Fe^{II}TMPyP]$^{5+}$ those modes follow the same pattern of the corresponding porphyne vibrations, exhibiting a minimum around 480 nm in the excitation profile.

As one can see in Figure 1.B a strong enhancement of the porphyrin vibrational modes is observed when the exciting frequency approaches that of the Soret band. The enhancement is less pronounced at the α and β bands.

A careful examination of the Raman intensities of (1) indicates two types of excitation profiles, one characteristic of the porphyrin system, with a minimum around 480 nm, and another one, associated with the pyridine vibrational frequencies at 1609, 1248, 1212 and 1027 cm^{-1}, which exhibit an additional enhancement around 480 nm. This observation is consistent with the presence of two chromophores in the totally reduced species, located at the porphyrin and at the $[Ru^{II}(edta)(pyP)]^{2-}$ peripheral groups, respectively. When the laser radiation is in resonance with the MLCT transition in the ruthenium(II) complexes, the pyridine vibrational peaks are selectively enhanced. In this way the rR spectra has provided a strong support for the assignment of the MLCT band at 480 nm in the multibridged porphyrin complex.

ACKNOWLEDGEMENTS

We gratefully acknowledge the support from CNPq, FAPESP and PADCT.

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Date Received: April 28, 1993
Date Accepted: June 9, 1993