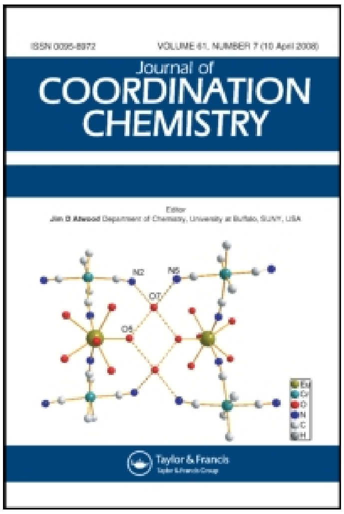
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

ELECTROCHEMICAL STUDIES OF THE BIMETALLIC COMPLEX FORMED BY RUTHENIUM(II) POLYPYRIDINE AND MANGANESE(III) PORPHYRIN

Marcos M. S. Paula[a]; César V. Franco[a]
[a] Laboratório de Química Biomimética (LQB) Depto. de Química, UFSC, Florianópolis, Brazil

To cite this Article Paula, Marcos M. S. and Franco, César V.(1995) 'ELECTROCHEMICAL STUDIES OF THE BIMETALLIC COMPLEX FORMED BY RUTHENIUM(II) POLYPYRIDINE AND MANGANESE(III) PORPHYRIN', Journal of Coordination Chemistry, 36: 3, 247 — 258

To link to this Article: DOI: 10.1080/00958979508022567

URL: http://dx.doi.org/10.1080/00958979508022567

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Coord. Chem., 1995, Vol 36, pp. 247–258
Reprints available directly from the publisher
Photocopying permitted by license only

© 1995 OPA (Overseas Publishers Association)
Amsterdam B.V. Published under license by
Gordon and Breach Science Publishers SA
Printed in Malaysia

ELECTROCHEMICAL STUDIES OF THE BIMETALLIC COMPLEX FORMED BY RUTHENIUM(II) POLYPYRIDINE AND MANGANESE(III) PORPHYRIN

MARCOS M.S. PAULA and CÊSAR V. FRANCO

Laboratório de Química Biomimética (LQB) Depto. de Química, UFSC, CEP 88040-900, Florianópolis, Brazil

(Received May 16, 1995; in final form June 26, 1995)

Downloaded At: 16:31 23 January 2011

In this communication we present results on the synthesis and characterization of a new *meso*-(5-(4-pyridil) 10, 15, 20 triphenyl porphyrinate) chloro manganese (III) porphyrin (ClMnP(Ph)$_3$py) modified with one $[(H_2O)Ru(bpy)_2]^{2+}$ group coordinated with the pyridine on the *meso*-position of the porphyrin ring. The resulting bimetallic complex was characterized by resonance Raman, IR, far-IR and electronic spectroscopy. Cyclic voltammograms of this monoruthenated porphyrin compound in acetonitrile exhibit three reversible waves at 1.53, 0.96 and 0.03V *vs* NHE. Spectroelectrochemical experiments were performed in acetonitrile and dimethyl sulfoxide and the results are in agreement with the cyclic voltammetric results. The anodic peak current of the cyclic voltammogram waves of the manganese porphyrin moiety in the monoruthenated compound was suppressed in the presence of atmospheric oxygen. These results provide evidence for an associative process of O_2 with the Mn(III) center of the porphyrin.

KEYWORDS: polypiridyl ruthenium, metallo porphyrin, electrochemistry

INTRODUCTION

Successful synthesis of a stable catalyst system for substrate oxidation could be very beneficial for solving the energy problem as it may provide an artificial photosynthetic system capable of generating and storing high energy chemical compounds.[1-2] The use of macrocyclic metal complexes for catalyzed reduction of O_2 to produce H_2O or H_2O_2 has been the focus of several researchers.[3-6] Among these compounds, metalloporphyrins have proved to be the most promising for catalyzed reduction of O_2. Manganese porphyrins have also proved to be efficient catalysts in reduction of oxygen. Several studies have shown that Mn(II), during the reaction, was converted to an intermediate Mn(V) species[7,8] or to a mixed-valence dimeric manganese Mn (III)/Mn (IV) complex.[9] The porphyrin compounds have a special advantage over other macrocyclic metal complexes due to their stability in acidic media and their physicalchemistry properties being sensitive to the substituent on the *beta* or *meso* ring position.[10-12] To obtain a molecular system capable of

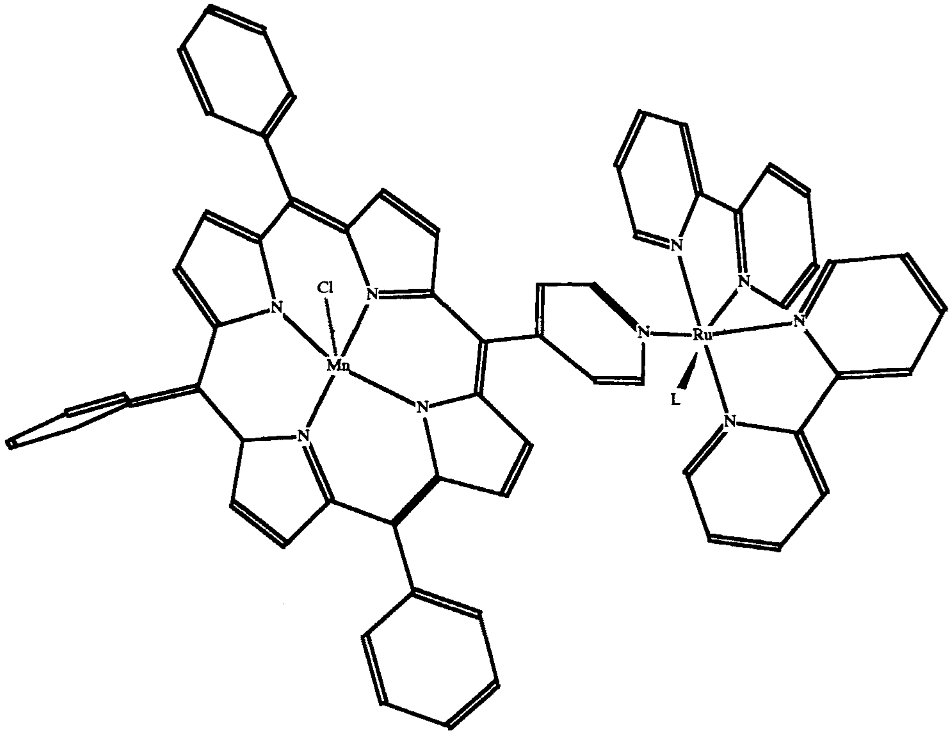
---

* Author for correspondence.

performing electrocatalytic reactions, several authors synthesized ruthenated porphyrins with ruthenium complexes coordinated on the *meso* position of the porphyrin ring.[13–15] Recently, Anson, *et al.*[13–14] examined the dependence of the catalytic activity of $(H_2O)Ru^{II}(NH_3)_5$ and $Ru^{II}(edta)^{2-}$ attached to the *meso*-position of the cobalt tetraarylporphyrins. Anson[14] considered the reducing ability of the ruthenium complexes along with their ability to back bond to pyridine as the probable cause for the improved electroreduction of dioxygen by cobalt porphyrin. In this sense, it was suggested that back bonding of the ruthenium rather than its oxidizability plays an important role in the enhanced catalytic activity. In addition, Ru^{II} $(edta)^{2-}$ shows negligible catalytic activity compatible with its poor back bonding to the pyridine ligand in spite of the fact that this complex is a strong reducer. As part of a large project where the main goal is to modify the porphyrin in order to improve catalytic activity, we began synthesis of a new class of binuclear complexes where two moieties are bridged through coordination between the *cis* - $[Ru(bpy)_2Cl_2].2H_2O$ complex, where bpy = 2,2'-bipyridine, and a (5-(4-pyridyl)-10, 15, 20-triphenilporphyrinate) chloro manganese (III) complex (ClMnP(Ph)$_3$py-) yielding the binuclear complex of the general structure I.

In this paper, we present preliminary results, on the synthesis, characterization and electrochemical behaviour of this new compound.

Downloaded At: 16:31 23 January 2011



STRUCTURE I

EXPERIMENTAL

Chemicals

All solvents and reagents were purchased commercially and used without further purification. The base 5-(4-pyridyl)-10,15,20-triphenylporphyrinate) porphyrin and the manganese (III) derivatives were synthesized as previously described.[16,17] The complex *cis*-$[Ru(bpy)_2Cl_2]\cdot 2H_2O$ was prepared according to the literature.[18] The bimetallic adduct was obtained according to a description in the literature with minor modifications.[19] A 10% excess of (5-(4-pyridyl)-10,15,20-triphenylporphirinate) chloro manganese (III) was dissolved in methanol and added to a warm (1:1) methanol/water solution of *cis*-$[Ru(bpy)_2Cl_2]\cdot 2H_2O$ and submitted to reflux in an argon atmosphere for 24h. After cooling an aqueous solution of NH_4PF_6 was added to yield a precipitate. Good crystals were obtained from slow diffusion of diethylether in acetonitrile.

Downloaded At: 16:31 23 January 2011

Analytical Measurements

The CHN elemental analyses were compatible with the theoretical composition: $RuMnC_{63}H_{54}N_9ClO_4P_2F_{12}$ (%) C, 51.14; H, 3.47; N, 8.52 Experimental (%) C, 51.06; H, 3.34; N, 8.21. The reproducibility of these results was checked with crystals from different syntheses. Thermogravimetric results confirmed the presence of four molecules of water (three hydrated molecules and one coordinated molecule) amounting to 4.9–5.1% by weight. Manganese content was analyzed by atomic absorption using as a standard $ClMnP(Ph)_4$ in concentrations ranging from 2 to 14 ppm. The found value of manganese (3.70%) is in good agreement with the theoretical value (Mn 3,71%). The found ratios of two PF_6^- counter-ions for each molecular adduct was determined by a conductivimetric method using a calibration curve obtained from well-known concentrations of *cis*-$[Ru(bpy)_2py_2](PF_6)_2$.

Spectroscopic Measurements

The electronic spectra were obtained with a Hewlett Packard spectrophotometer model HP8452A. The infra-red and far infra-red spectra were recorded on a Perkin-Elmer model 1GPC FT-IR and Perkin-Elmer model 180, respectively. The resonance Raman spectra were recorded at the Laboratory of Molecular Spectroscopy (Instituto de Química de Universidade de São Paulo, USP) with a Javel-Ash 25-300 equipped with a double monochromator. The measurements were performed in the preresonance region ($\lambda_{exc} = 514.5$ nm, from an Argon Laser).

Spectroelectrochemical Measurements

The Optically Transparent Thin Layer Electrode (OTTLE) experiments[20] were performed using a Hewlett Packard spectrophotometer model HP8452A for optical monitoring and a Pine Instrument Company bipotentiostat model RDE4 for electrochemical control.

Electrochemical Measurements

The cyclic voltammetry measurements were carried out at 25°C with a Princeton Applied Research (PARC) Model 273A Potentiostat/Galvanostat interfaced with a DOS compatible computer through a National Instrument General Purpose Interface Board (GPIB). To minimize the *i*R ohmic drop, the resistance compensation feature of the instrument was employed in all measurements and a lugging capillary was employed. A conventional electrochemical cell was used. A platinum electrode (area 0.115 cm^2) served as working electrode. A platinum wire and $Ag/AgNO_3$ (0.1 M) in acetonitrile (0.503V *vs* NHE) served as the counter and reference electrode, respectively. The performance of the reference electrode was monitored by testing against a commercial SCE electrode using a 3/1/2 digit voltammeter. The measured difference of < 40 mV between the two reference electrodes is acceptable. As support electrolyte, 0.1 M tetrabutylammonium hexafluorophosphate (HTBA) in acetonitrile was employed. All electrochemical experiments that demanded an inert atmosphere were performed in a glove bag filled with ultrapure grade argon.

Analytical Instrumentation

The thermogravimetric analyses were performed on a Shimadzu Thermogravimetric Analyzer model TGA-50. The atomic absorption measurements were recorded on a Hitachi Atomic Absorption Spectrophotometer model Z8230 Polarized Zeeman. The elemental analyses were performed on a Perkin-Elmer CHN analyzer model 2400. The magnetic measurements were performed on the Johnson-Matthey balance for room temperature measurement.

Downloaded At: 16:31 23 January 2011

RESULTS AND DISCUSSION

Analytical measurements and magnetic features

Elemental CHN analyses, thermogravimetric analyses, and atomic absorption measurements suggest a binuclear complex with one ruthenium center attached to a *meso*-pyridil on the chloro manganese porphyrin ring. The presence of two PF_6^- counterions indicates at first glance, a binuclear complex with one chloride ligand probably coordinated at the manganese(III) center and a water molecule coordinated at the ruthenium (II) center. Alternatively, the ruthenium(II) could be coordinated by the chloride and Mn(III) coordinated by a water molecule. The unexpected charge could also be explained by the presence of a manganese(III) porphyrin π-cation radical species. All of these alternatives gave almost identical elemental analyses. The assignment of a Mn(III) π-cation radical could be based on evidence from magnetic susceptibility of the solid. The magnetic susceptibility measurements at room temperature (after correction for a diamagnetic contribution) gave a value of the effective magnetic moment = 5.66 μB for a spin only system. This is above the measured value[20] of μ_{eff} = 4.81 μB for the $ClMnP(Ph)_4$ and below the calculated value of μ_{eff} = 5.91 μB for the radical cation.[2] The possibility of both, spins for d^4 (S = 2) associated with an independent spin (S = 1/2) on the oxidized porphyrin ring, μ_{eff} = 5.19 μB and antiferromagnetic coupling μ_{eff} = 3.87 μB is also ruled out. Temperature dependent magnetic susceptibility and

EPR spectroelectrochemical measurements are under way to better characterize the magnetic features of this new binuclear complex. The cation radical could also be supported from a resonance Raman spectroscopy due to the presence of a peak at 1020 cm^{-1} that was reported[21] only in radical cation spectra of ClFeTPP. In addition we have other evidence favoring the compound [ClMnP(Ph)$_3$py {Ru(bipy)$_2$H$_2$O}](PF$_6$)$_2$·3H$_2$O (Structure **1**). The following discussion emphasizes results from IR, far-IR, and RR spectroscopy, electronic absorption spectroscopy and electrochemical experiments which strongly support the proposed structure **1**.

IR and far-IR spectra

Figure 1 shows the FT-IR spectra of [ClMnP(Ph)$_3$pyRu(bipy)$_2$Cl]$^{2+}$ along with the spectra of ClMnP(Ph)$_3$py and Ru(bipy)$_2$Cl$_2$. The IR spectra showed the counterion PF_6^- at 842 cm^{-1}. The far-IR spectra showed the usual axial ν(Mn-Cl) stretching band[22] at 258 cm^{-1} as well as a ν (Ru-OH$_2$) stretching band presumably due[23] to the axial ligand at 278 cm^{-1}. IR and far-IR absorption spectra of the complex were determined for both KBr and CsI pellets.

Downloaded At: 16:31 23 January 2011

RR Spectra

Figure 2 summarize the resonance Raman spectroscopic data. The spectra of the adduct show features clearly due to both moieties. In Figure 2, the modes at 664, 1170 1485, 1557, 1320 and 1600 cm^{-1} are characteristic to the bpy ligand.[24] The modes at 1090, 1185, 1265, 1367, 1498 and 1580 cm^{-1} were assigned by analogy to those of H$_2$TPP[25–26] and CuTPP[27,21] and are characteristic of ClMnP(Ph)$_3$py. The RR spectrum contains new absorbance bands (*vs.* MnClP(Ph)$_3$py and Ru(bipy)$_2$Cl$_2$) at 238, 310 and 495 cm^{-1}.

Electronic Absorption Spectra

Figure 3 shows a typical electronic spectrum of the monoruthenated porphyrin in acetonitrile. The absorption bands at 246, 294, 374, 398, 470, 474, 576 and 616nm, and are consistent with the presence of both moieties. The bands corresponding to the porphyrinic moiety at 374 and 392nm are assigned to the split Soret band; the band located at 474nm corresponds to a charge transfer band. Q bands at 576 and 616nm were also found. The absorption band at 294nm can be ascribed to a π - π^* transition in the bpy ligand, while the band at 470nm refers to a transition Ru^{II}-π^*(bpy), both assigned to the ruthenium moiety. The visible spectra of ClMnP(Ph)$_3$py in *cis*-[ClMnP(Ph)$_3$pyRu(bpy)$_2$(H$_2$O)]$^{2+}$ only shifts band position slightly when compared with [ClMnP(Ph)$_3$py. This suggests that the presence of ruthenium at the *meso* position of the porphyrin only slightly affects the porphyrin π and σ system. The bands at 246 and 470nm, obtained by subtraction of electronic spectra of *cis*-[ClMnP(Ph)$_3$pyRu(bpy)$_2$H$_2$O]$^{++}$ from ClMnP(Ph)$_3$py, correspond to those described by the literature[28] for [Ru^{II}(bpy)$_2$pyH$_2$O]$^{2+}$. The electronic spectrum was also measured in DMSO and bands at 298, 396, 376, 396, 466, 568, 604 nm were found. Valentine and Quinn[29] assigned the bands at 466, 568 and 604 nm to a dissociated form of MnTP$^+$ that coordinates DMSO.[30] The

Downloaded At: 16:31 23 January 2011

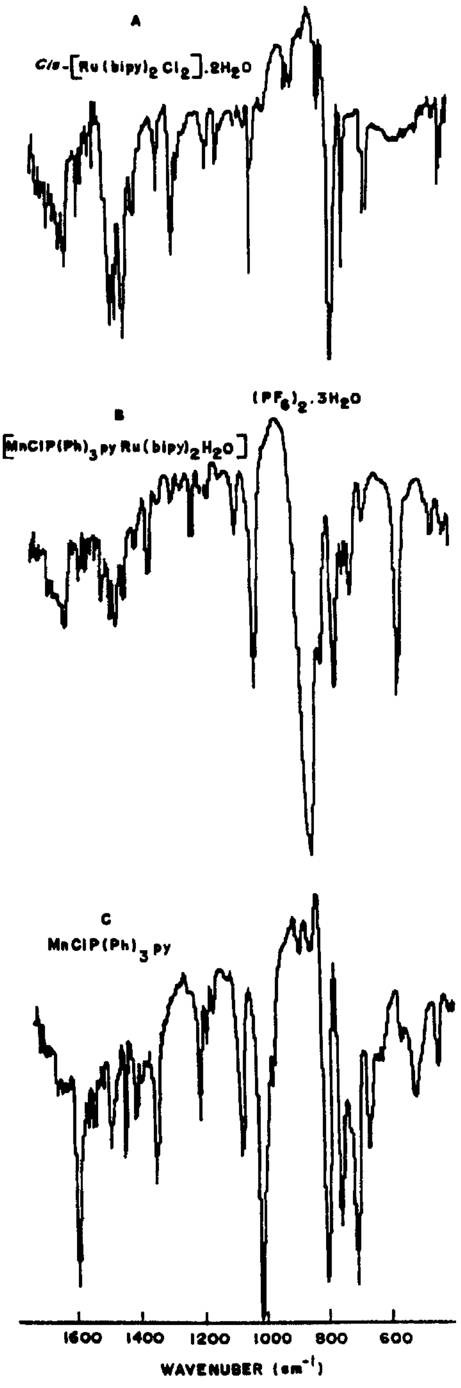


Figure 1 Infrared Spectra of [MnP(Ph)$_3$py{Ru(bipy)$_2$H$_2$O}](PF$_6$)$_2$ and its components in KBr pellets.

Downloaded At: 16:31 23 January 2011

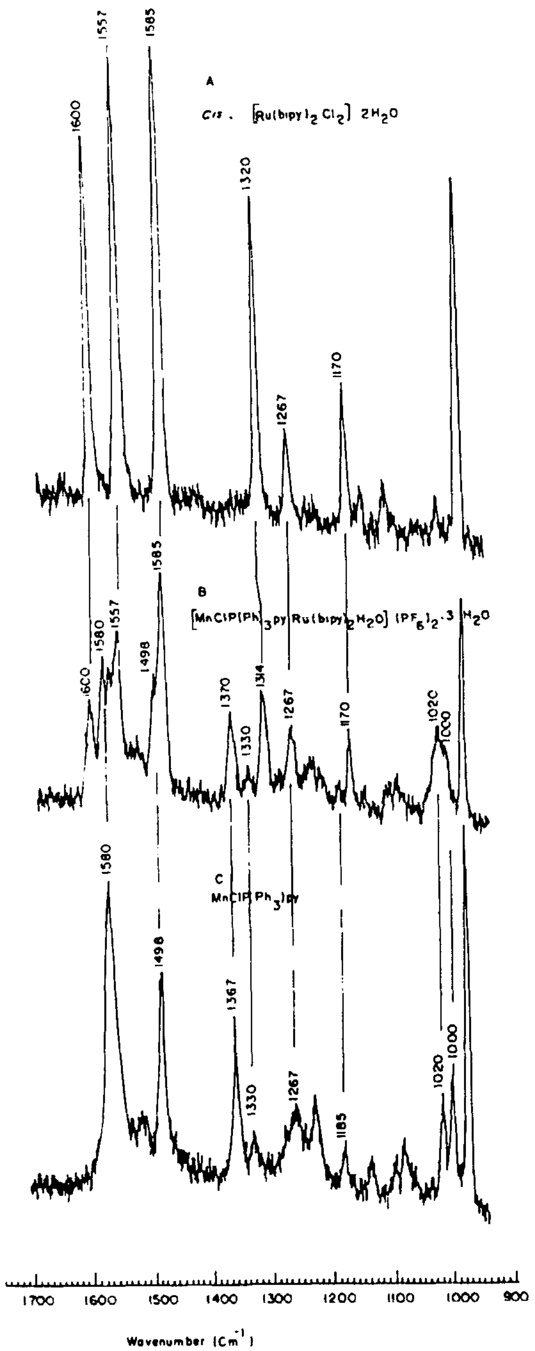


Figure 2 Resonance Raman spectra of $[MnP(Ph)_3py\{Ru(bipy)_2H_2O\}](PF_6)_2$ and its components. Spectra were obtained with 514.5 nm excitation and samples diluted in K_2SO_4.

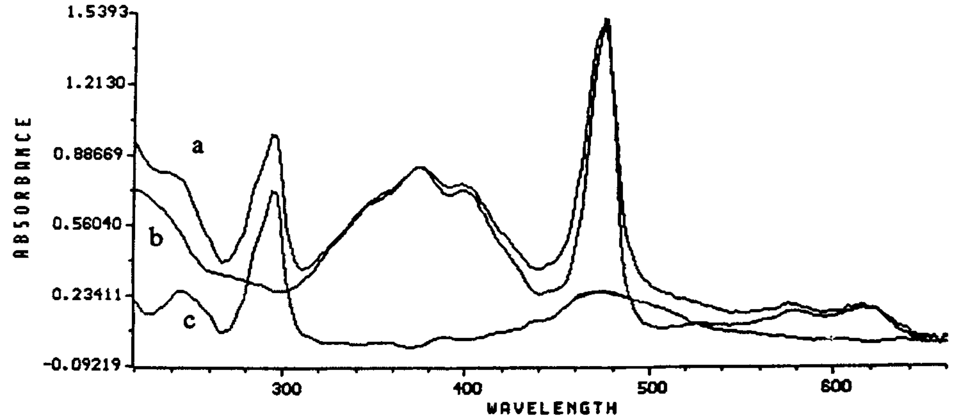


Figure 3 Electronic spectra in acetonitrile of (a) $[MnClP(Ph)_3py\{Ru(bipy)_2H_2O\}](PF_6)_2$ (b) $MnClP(Ph)_3py$ and (c) electronic spectral substraction of a - b.

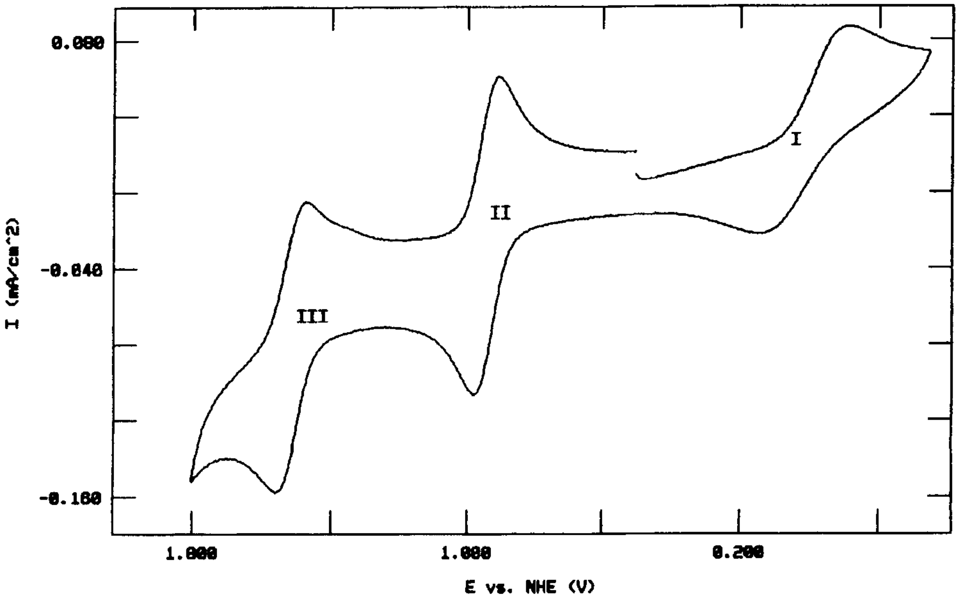


Figure 4 Cyclic voltammogram of 0.5 mM of $[MnClP(Ph)_3py\{Ru(bipy)_2H_2O\}](PF_6)_2$ acetonitrile, 0.1M $TBAPF_6$, scan rate 20 mVs^{-1}.

band positions of porphyrinic fragments, in analogy to results in the literature,[31] shows a dependence on solvent and concentration.

Electrochemistry

Cyclic voltammetry of the binuclear porphyrin complex in acetonitrile, under a

Downloaded At: 16:31 23 January 2011

Downloaded At: 16:31 23 January 2011

rigorously inert atmosphere, exhibits three characteristic oxidative waves at 0.03 V (I), 0.96(II) and 1.53(III) *vs.* NHE within the solvent limits, as shown in Figure 4. The first oxidative wave at 0.03V ($i_{pa}/i_{pc} = 0.90$, $Q_a/Q_c = 0.91$) can be assigned to the chloro manganese (III) porphyrin moiety, due to the redox couple Mn^{III}/Mn^{II}, by analogy with $ClMn(Ph)_3py$.[12,20] This reaction is electrochemically quasireversible with ΔEp of 200 mV at 100 mVs^{-1}. According to Mu and Schultz[12] the slow electron transfer associated with the Mn^{III}/Mn^{II} couple is the result of a large difference in structure between Mn(II) and Mn(III). The reversible wave(II) at 0.96 V (ΔE_p = 70 mV, i_{pa}/i_{pc} = 1.00, Q_a/Q_c = 1.00) follows the Randles-Sevcik equation for a monoelectronic process and can be assigned to oxidation of the metal

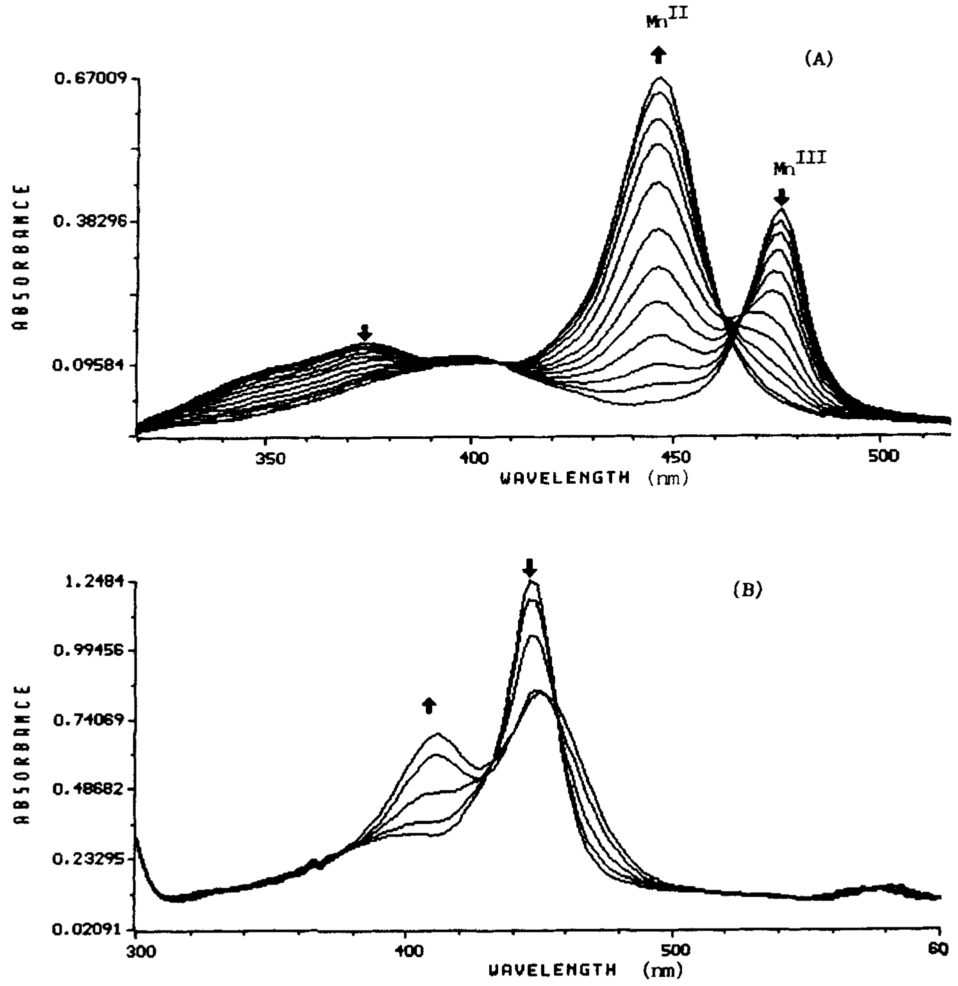


Figure 5 Spectro-electrochemistry of $[MnP(Ph)_3py\{Ru(bipy)_2H_2O\}](PF_6)_2$ in acetonitrile. (a) reduction of Mn(II) at potentials ranging from 0.1 to -0.20V, (b) reduction of Ru(II) at potentials ranging from −0.6 to −1.1 V.

Downloaded At: 16:31 23 January 2011

center and formation of low-spin ($4d^5$) Ru^{III}. The formal potentials are shifted in the negative direction by 80 mV as compared to those reported in the literature[28] for $[Ru^{II}(bipy)_2PyH_2O]^{2+}$ in 1.0 M $HClO_4$. The integrated areas under the waves of peak potentials from the differential pulse voltammetry at 0.03 V (I) and 0.96(II) give us the total charge (mC) involved in the process. The values of 0.28(I) and 0.23 mC.cm^{-2} (II) clearly indicate a manganese/ruthenium ratio of 1:1. This provides strong support for the proposed composition. The same ratio was also found when crystals were analyzed under the microprobe (electron diffraction X-ray) EDX technique. The value of almost unity for the charge ratio from the cathodic to anodic peaks indicates the chemical reversibility of the system. The reversible wave at 1.53 V (ΔE_p = 88mV, i_{pa}/i_{pc} = 0.96, Q_a/Q_c = 0.93) corresponds to the first oxidative process in the porphyrin ring.[12] Data from differential pulse voltammetry

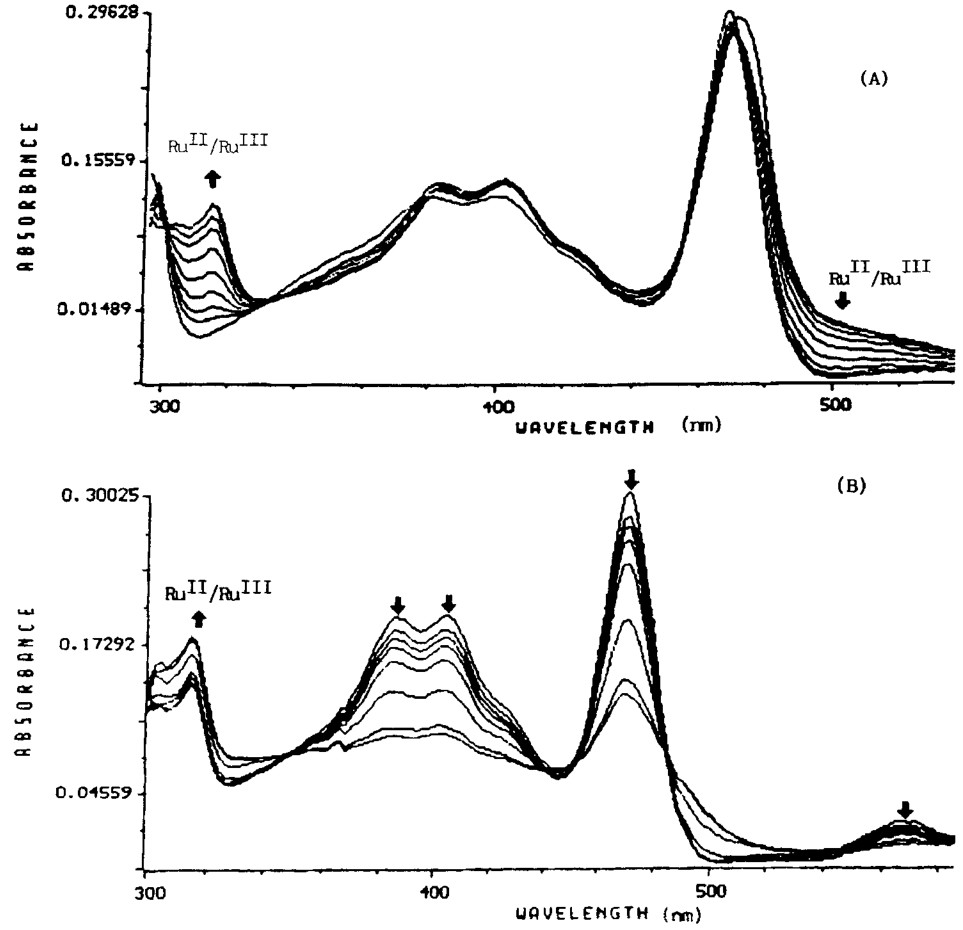


Figure 6 Spectro-electrochemistry of $[MnP(Ph)_3py\{Ru(bipy)_2H_2O\}](PF_6)_2$ in acetonitrile. (a) oxidation of Ru(II) at potentials ranging from 0.94 to 1.10V, (b) oxidation of Mn(II) at potentials ranging from 1.30 to 1.70V.

show the first oxidation process as a sharp peak at 1.54V. Reversibility in the redox reaction of the porphyrin ring is observed in other reactions of porphyrin and results from the small structural change of the ring.[12] Controlled potential coulometric experiments were performed on the reduction of Mn(III) and oxidation of Ru(II) to confirm an electrochemical process involving consumption of one electron/molecule.

Spectro-Electrochemistry

The spectro-electrochemical results for reduction of monoruthenated porphyrin in acetonitrile, are shown in Figure 5a and b. To perform the reduction on the manganese(III) center in acetonitrile solution, $E_{applied}$ was varied from 0.10 to -0.20V which leads to suppression of the Mn^{III} CT band at 474 nm and the appearance of a new band for a Mn^{II} at 448nm. The bands in the visible region remain unchanged. The same spectral pattern was found upon reduction of ClMn(III)TPP.[20] For values of $E_{applied}$ in the range from -0.6 to -1.1V (Fig. 5b) a slight decrease of the band at 446nm and the appearance of a new band at 410nm were observed corresponding to reduction of the porphyrin ring with a formed π-anion species. In addition, the bands at 568 and 604nm undergo a reduction in intensity and a bathochromic shift of around 10 nm. These results correlate with those of the spectro-electrochemistry of the non-modified MnCl(Ph)3pyP species.[20] For $E_{applied}$ in the range 0.94V to 1.10V (Fig. 6a), there is a splitting of the band at 298nm and the appearance of two new bands at 304 and 314nm, due to oxidation of the Ru^{II} center. The band at 470 nm gradually disappears, along with the splitting of the bipyridine band at 298 nm into two bands with maxima at 304 and 314 nm. The charge transfer shifts from 474 to 468 nm upon ruthenium oxidation, and decreases in intensity by 9%. The same splitting of the bpy ligand absorption band has been reported for reduction of $[Ru(bpy)_2pyCl]^+$ in the tetraruthenated porphyrin.[31] Spectroelectrochemical experiments performed in the reverse way, clearly demonstrated the reversibility of the redox system with the reappearance of Ru^{II}. The process can be repeated several times and shows good reproducibility. At more positive values of $E_{applied}$ from 1.30 to 1.70 V (Fig. 6b), a constant decrease in the intensity of bands at 386 and 404nm was observed along with a slight diminishing of a band at 470 nm. Isosbestic points occur at 548, 484, 452, 440, 348nm. The spectro-electrochemical experiment was also performed in DMSO and in this case there is a suppression of the CT band at 466 nm and appearance of a new band at 442 nm upon reduction of the manganese(III) center.

Experiments conducted at the cathodic region, (potentials in the range 0.94 to 1.10V) lead to a plot of $E_{applied}$ *vs.* Log ([O]/[R]) with values for $E_{1/2}$ of -0.01V, close to those obtained from CV and VDP. A transfers of one electron molecule was estimated at this potential.

In conclusion, we have demonstrated from electrochemical and spectro-electrochemical results, that $[\text{-}Ru(bpy)_2H_2O1]^{2+}$ attached to the porphyrin is consistent with a redox system that interacts only weakly. Detailed electrochemical studies on oxygen activation toward olefin epoxidation by electrolytic reduction of this, and related, ruthenated porphyrins are underway in order to exploit their potential as electrocatalyst.

Downloaded At: 16:31 23 January 2011

Acknowledgement

Financial support was provided by CNPq contract # 40 08 47 93 0 - QUE. We are indebted to Prof. Adilson Curtius for performing the atomic absorption experiments as well as to Prof. Norberto Sanches for RR and far-IR measurements. The authors would like to acknowledge Prof. Oswaldo Sala for allowing the use of RR and far-IR facilities.

References

1. M. Calvin, *Photochem. Photobiol.*, **37**, 349 (1986).
2. L.O. Spreer, A.C. Maliyackel, S. Holbrook, J.W. Otvos, and M. Calvin, *J. Am. Chem. Soc.*, **108**, 1949 (1986).
3. M. Jahnke, M. Scohonbron, and G. Zimmerman, *Top. Curr. Chem.*, **61**, 133 (1980).
4. R.D. Jones, D.A. Summerville, and F. Basolo, *Chem. Rev.*, **70**, 39 (1979).
5. L.J. Boucher, in C.A. Melson (Ed.), *Coordination of Macrocyclic Compounds*, (Plenum Press, New York, 1979) p. 461.
6. Y. Olivier Su, T. Kuwana, and S. Chen, *J. Electroanal. Chem.*, **28**, 177 (1990).
7. S.E. Creager, S.A. Raybuck, and R.W. Murray, *J. Am. Chem. Soc.*, **10**, 4225 (1986).
8. S.E. Creager, and R.W. Murray, *Inorg. Chem.*, **26**, 2612 (1987).
9. M. Perree-Fauvet, A. Gaudemer, J. Bonvoisin, J.J. Girerd, C. Boucly-Goester, and P. Boucly, *Inorg. Chem.*, **28**, 3533 (1989).
10. F.P. Dwyer, H.A. Goodwin, and E.C. Gyarfas, *Aust. J. Chem.*, **16**, 544 (1963).
11. B.A. Moyer, and T.J. Meyer, *J. Am. Chem. Soc.* **100**, 3601 (1978).
12. Xi. Hai Mu, and F.A. Schultz, *Inorg. Chem.*, **29**, 2879 (1990).
13. C. Shi, and F.C. Anson, *J. Am. Chem. Soc.*, **113**, 9564 (1991).
14. B. Steiger, C. Shi, and F.C. Anson, *Inorg. Chem.*, **32**, 2107 (1993).
15. H.E. Toma, and K. Araki, *J. Chem. Res.*, **82**, (1990).
16. E.B. Fleischer, and A.M. Shachter, *Inorg. Chem.*, **30**, 3763 (1991).
17. A.D. Alder, F.R. Longo, F. Kampas, and J. Kim, *Inorg. Nucl. Chem.*, **32**, 2443 (1970).
18. B.P. Sullivan, D.J. Salmon, and T.J. Meyer, *Inorg. Chem.*, **17**, 3334 (1978).
19. F.P. Dwyer, H.A. Goodwin, and E.C. Gyarfas, *Aust. J. Chem.*, **16**, 544 (1963).
20. M.M.S. Paula, and C.V. Franco, *Quimica Nova,* Vol 17 No. 5 (1994).
21. R.S. Czernuszewicz, K.A. Macor, X.-Y. Li, J.r. Kincaid, and T.G. Spiro, *J. Am. Chem. Soc.*, **111**, 3860 (1989).
22. L.J. Boucher, *J. Am. Chem. Soc.*, **92**, 2725 (1970). 23- P.A. Mabrouk, and M.S. Wrighton, *Inorg. Chem.*, **25**, 526 (1986).
23. The compound *cis*-[(H_2O)(isonicotinic acid) Ru $(bipy)_2$](PF_6) has been recently synthesized and characterized in our laboratory showing two far-IR bands at 277 and 253 cm^{-1}. Comparatively the *cis*-[$Cl_2Ru(bipy)_2$] show two bands at 258 and 239 cm^{-1}.
24. P.A. Mabrouk, and M.S. Wrighton, *Inorg. Chem.*, **25**, 526 (1986).
25. S.E.J. Bell, A.H.R. Al-Obaidi, M. Hegarty, R.E. Hester, and J.J. McGarvey, *J. Phys. Chem.*, **97**, 11599 (1993).
26. X.-Y. Li, and M.Z. Zgierki, *J. Phys. Chem.*, **95**, 4268 (1991).
27. S. Hu, and T. G. Spiro, *J. Am. Chem. Soc.*, **115**, 12029 (1993).
28. B.A. Moyer, and T.J. Meyer, *J. Am. Chem. Soc.*, **100**, 3601 (1978).
29. J.S. Valentine, and A.E. Quinn, *Inorg. Chem.*, **15**, 1997 (1976).
30. B. Gonzales, J. Kouba, S. Yee, C.A. Reed, J.F. Kirner, and W.R. Scheidt, *J. Am. Chem. Soc.*, **97**, 3247 (1975).
31. E. Van Cacmelbecke, W. Kutner, and K.M. Kadish, *Inorg. Chem.*, **32**, 438 (1993).
32. K. Araki, and H.E. Toma, *J. Coord. Chem.*, **30**, 9 (1993).

Downloaded At: 16:31 23 January 2011